

ATTEMPTS TO GENERATE A HOMOAROMATIC CARBENE
AND BISNORCARADIENE

By

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The great tragedy of Science [is] the slaying of a
beautiful hypothesis by an ugly fact.

Thomas Henry Huxley

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Abstract of Dissertation Presented to the Graduate
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Fulfillment of the Requirements for the
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ATTEMPTS TO GENERATE A HOMOAROMATIC CARBENE
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by

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Chairman: W. M. Jones
Major Department: Chemistry

A neutral homoaromatic species has not been reported in the chemical literature. The similarity of the charge separated resonance structure of 2,5,7-cyclooctatrienylidene, 1, to the structure of the homotropylium ion implies that this carbene might be a good candidate for a neutral homoaromatic species.

The chemistry of the parent aromatic system, cycloheptatrienylidene, suggests two methods of generating 1. Base induced dehydrohalogenation of 5-chlorobicyclo[5.1.0]-2,4-octadiene or 5-chlorobicyclo[5.1.0]2,5-octadiene should yield an allene that could rearrange to the carbene, 1. This carbene could also result from the carbene-carbene rearrangement of 2- and 3-cycloheptatrienylcarbene. In this study, the chlorides could not be generated and attempts to generate the cycloheptatrienylcarbenes resulted in pyrazoles.

The cyclopropene, 2,4,8-bicyclo[5.1.0]octatriene, 2, is the intermediate that would be expected in the carbene-carbene rearrangement of the cycloheptatrienylcarbenes mentioned above. This species was generated from the reaction of trans-8-chlorobicyclo[5.1.0]2,4-octadiene with potassium t-butoxide and trapped with diphenylisobenzofuran. In the absence of trapping materials, this reaction yielded cyclooctatetraene, heptafulvene and a trace of styrene.

It is postulated that the cyclopropene, 2, rearranges to 1, which inserts into one of the transannular methylene C-H bonds to yield 2,4,7-bicyclo[4.2.0]octatriene. This species opens in its usual manner to yield cyclooctatetraene. It is proposed that the other two products are the result of a base induced isomerization of 2 to 1,3,5-bicyclo[5.1.0]octatriene. This either undergoes electrocyclic ring opening to heptafulvene or a norcaradiene rearrangement to a bicyclobutene, which opens to styrene.

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene in the same manner seems to follow a similar pathway. The only products isolated from this reaction were 8-bromoheptafulvene, trapped with diphenylisobenzofuran, and β -t-butoxystyrene. No bromocyclooctatetraene was noted, although the cyclopropene precursor is definitely formed since it was trapped with diphenylisobenzofuran. The styrene ethers appear to have been formed from a small amount of starting material that was able to doubly dehydrohalogenate.

An attempt was also made to synthesize bisnorcaradiene, 2,4,8,10-tricyclo[5.4.0.0^{1,6}]undecatetraene, 3. Cycloheptatetraene was allowed to react with 2-pyrone to yield, ultimately, 3,4-benzocycloheptatriene, 4. This reaction is postulated to proceed through an intermediate pentaene, 1,3,5,8,10-bicyclo[5.4.0]undecapentaene, 5. These pentaenes, when substituted, are believed to undergo electrocyclic ring closures to bisnorcaradienes. The ability of these bisnorcaradienes to open to pentaenes with different substitution patterns has led to the postulation of the intermediacy of bisnorcaradienes in many chemical reactions in which substituent scrambling of this type was noted. When a deuterated 2-pyrone was allowed to react with cycloheptatetraene, substituent scrambling of the type mentioned above did not occur. This reaction implies a competition between the ability of 5 to close to 3 and the ability of 5 to aromatize to 4 previously not noted.

ATTEMPTS TO GENERATE A HOMOAROMATIC CARBENE

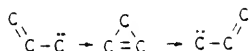
Introduction

Cycloheptatrienylidene¹ is an example of an aromatic carbene. It appears that the vacant p orbital of the singlet carbene has electron density from the six pi electron system delocalized into it, in much the same way that electron density is delocalized into the vacant orbital in the tropylium ion. The effect is evident in the reduced electrophilicity of the system compared to that of other carbenes lacking this conjugated pi system. The Hammett rho value of typical electrophilic carbene,² such as dichlorocarbene (-0.619 at 80°, -0.378 at 0°), differs drastically from that noted for this carbene (+1.05).² The increased stability of this carbene is also displayed in its lack of reactivity with alkenes not containing electron withdrawing substituents. In the absence of groups of this kind, the carbene merely dimerizes to heptafulvalene.



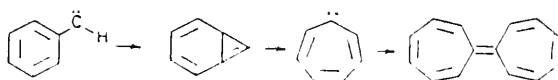
One of the more interesting properties of this carbene is its participation in carbene-carbene rearrangements.³ This reaction of carbenes is one in which a carbene at a vinylogous position can migrate to the adjacent carbon.

This interconversion of vinylcarbenes takes place through an intermediate cyclopropene. Closure of the vinyl carbene to the cyclopropene is a thermally allowed (2_s+2_a) cyclo-

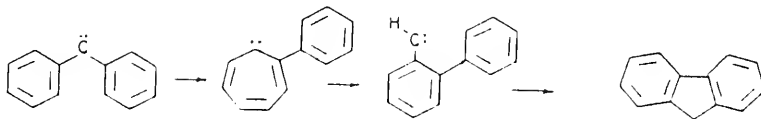


addition of the singlet carbene. Thermal opening of the ring along similar lines leads to the formation of the new vinylcarbene.

When phenylcarbene is generated at 250° in the gas phase,⁴ heptafulvalene is produced. This compound is postulated to arise from rearrangement of the phenylcarbene to cycloheptatrienyliene, through the bicyclic triene. The cycloheptatrienyliene then dimerizes as described above.

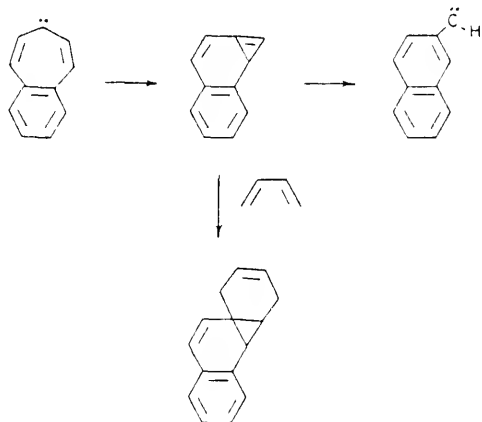


Rearrangements of substituted cycloheptatrienylenes to yield substituted phenylcarbenes have been noted also. Diphenylcarbene⁵ generated in the gas phase yields fluorene, presumably through a phenyl substituted cycloheptatrienyliene.



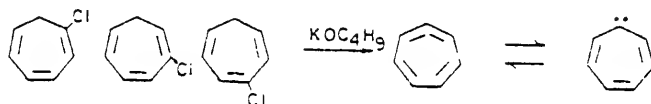
While the interconversion of phenylcarbene and cycloheptatrienyliene is a gas phase phenomenon, substitution of this parent system can result in carbene-carbene rearrange-

ments in solution. Decreasing the aromaticity of the aromatic carbene lessens the impact on the delocalization energy of the carbene when the cyclopropene intermediate is formed, thus facilitating the reaction. An example is the 4,5-benzocycloheptatrienyliene system in which an annelated ring is incorporated into the 4,5 bond of the cycloheptatriene moiety. When formed by either photolysis or thermolysis, it rearranges in solution to yield beta-naphthylcarbene.⁶ The annelated ring decreases the effect of the loss of aromaticity when the cyclopropene is formed. The cyclopropene intermediate in this reaction has been trapped in a Diels-Alder reaction with butadiene, cyclopentadiene, and furan.⁷

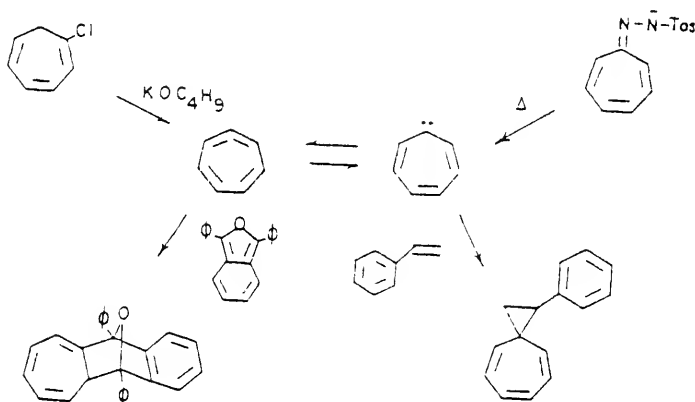


Another interesting feature of this carbene is its ability to equilibrate to its valence isomer, cycloheptatetraene.⁸ Untch has found that dehydrohalogenation of a mixture of 1-, 2-, and 3-chlorocycloheptatrienes yields heptafulvalene.⁹ This is proposed to proceed through an

initial dehydrohalogenation to the cyclic allene that isomerizes to the carbene, which dimerizes. The interconversion of these isomeric intermediates has been shown to be independent of their precursors. Regardless of whether these intermediates are generated from thermolysis of the sodium salt of tropone tosylhydrazide or the reaction of



the above mentioned chloride mixture with potassium *t*-butoxide,¹⁰ the allene can be trapped with isobenzofuran and the carbene can be trapped with styrene.



Homoaromaticity is a term coined by Winstein¹¹ to title the effect noted in some carbonium ions in which unusual stabilization is retained in ions in which conjugation has been interrupted in a pi system that would otherwise be aromatic. This effect, seen in many cationic species, has not been noted in neutral species.

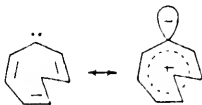
The interaction of the vacant p orbital with the pi system in cycloheptatrienylidene mimics the interaction of the vacant p orbital in the tropylium ion. Indeed, a resonance structure of this carbene can be drawn in which the tropylium ion is incorporated.



Homotropylium ions have been prepared and extensively studied.¹² The apparent structure of these ions seems to be that of a non-classical monocyclic system, although some arguments have been made toward a classical bicyclic system. This ion suggests that it may be possible to generate a carbene that would show this type of homoaromatic behavior.

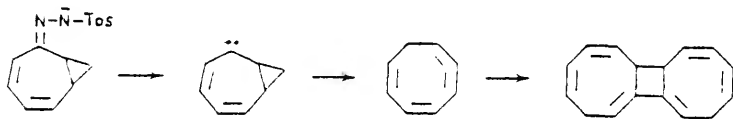


This neutral species, which would have a resonance structure that mimics the homotropylium ion, might be an exception to the generality that homoaromaticity is restricted to charged species.



There are two ways of studying the possibility of homoaromaticity in a cycloheptatrienylidene system. Replacing

one of the olefinic positions with a fused cyclopropane ring would yield a carbene that would be analogous to the bicyclic homotropylium ion above. This reaction has been carried out by Oda et al.¹³ When the sodium salt of bicyclo-[5.1.0]octa-3,5-dien-2-one tosylhydrazone was photolyzed or pyrolyzed, the ensuing carbene immediately underwent ring opening of the cyclopropane to yield 1,2,4,6-cyclooctatet-



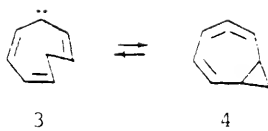
raene, which dimerizes under the reaction conditions.

The other possibility is to introduce a methylene insulating group into the pi system. This can be done in one of two positions to yield either 2 or 3. It would be expected that in isomer 2, the rapid 1,2 hydrogen migration to yield cyclooctatetraene would predominate over any



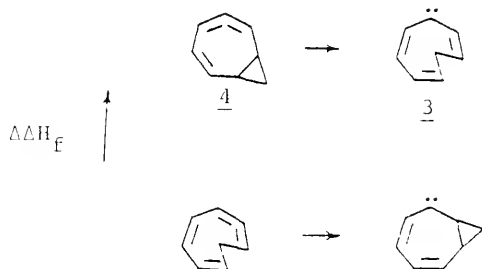
other carbene reaction. Isomer 3 cannot undergo this reaction.

The rearrangement of the carbene generated by Kitahara, to the allene, along with the known ability of cycloheptatetraene, to isomerize to cycloheptatetraene, suggests that isomerization of 3 to its allene form, 4, might be a dominant



reaction of this carbene. If this is so, then there would be no opportunity to observe the reaction of the carbene.

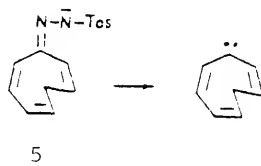
Arguments can be made that suggest that rearrangement of 3 to 4 may be less likely than the rearrangement of Kitahara's carbene to the corresponding allene. Calculation of the differences in the enthalpies of formation between these allenes and the corresponding carbenes were made using the group equivalents of Benson.¹⁴ Without correction for allene strain or any aromatic or homoaromatic stabilization, the difference in enthalpies ($\Delta\Delta H_f$) between 3 and 4 was shown to be 10 Kcal greater than the difference between Kitahara's carbene and allene. Intuition would lead to the notion that the strain in the seven membered ring of 4 would be greater than that in the eight membered ring of Kitahara's allene. This would imply a greater $\Delta\Delta H_f$ than



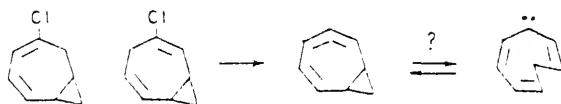
the calculations indicate. This $\Delta\Delta H_f$ between 3 and 4 is 5 Kcal greater than the corresponding difference in the enthalpies of formation of cycloheptatrienylidene and cycloheptatetraene, a system shown to be in equilibrium (vide supra). This would indicate that the rearrangement of the carbene, 3, to the allene, 4, would be more endothermic, or less exothermic, than the rearrangement noted by Kitahara, and less likely to occur.

The chemistry of cycloheptatrienylidene suggests three ways to generate the homoaromatic carbene, 3. The most straightforward would be from thermolysis or photolysis of the sodium salt of the tosylhydrazone of 2,5,7-cyclooctatrienone, 5.

If homocycloheptatrienylidene exists in equilibrium

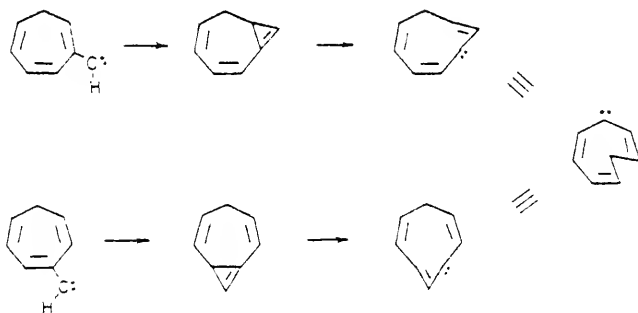


with an allene isomer, a second method might be possible to generate the carbene, through a dehydrohalogenation reaction similar to the one used to generate cycloheptatrienylidene. The allene isomer, 4, that would be the valence isomer of 3 could be generated from the dehydrohalogenation of the chlorides above.



The third possible pathway to the homoaromatic carbene is through a carbene-carbene rearrangement. The cycloheptatrienylcarbenes below have the opportunity to rearrange in a similar manner to that of phenylcarbene, to give 3. In principle, these carbenes could be generated by thermolysis or photolysis of the sodium salts of the tosylhydrazones of the corresponding aldehydes.

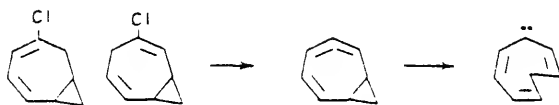
An evaluation of homoaromaticity in this system could



be carried out along the same lines as those used to study the aromaticity of cycloheptatrienylidene. If full or partial retention of the ability to delocalize the pi electron system into the vacant orbital of the carbene occurs, the system can be studied by the nucleophilicity of the carbene. Its ability to react with olefins reactive to normal electrophilic carbenes can be tested. The ideal study would be one in which the carbene is allowed to react with substituted styrenes and its Hammett rho value determined. This should give a quantitative measure of the nucleophilicity, i.e., the aromaticity, of the carbene.

Results and Discussion

Because of the lack of a feasible synthetic route to the sodium salt, 5, attempts were made toward the synthesis of 3 via the rearrangement of isomeric materials. Isomerization of the allene, 4, would be the simplest route. The required chlorides are simply the addition products of methylene to 1-chlorocycloheptatriene. Although this compound, free of other isomeric chlorides, has been synthesized by Untch,¹⁵ the synthesis requires many steps and results in a low yield. A more economical method of preparation

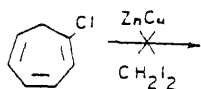


might be through separation of the isomers of 1-, 2-, and 3-chlorocycloheptatrienes, synthesized by Folisch¹⁶ from tropone. Reaction of this material with Simmons-Smith reagent should yield the desired compounds.



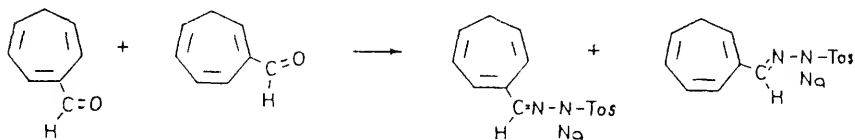
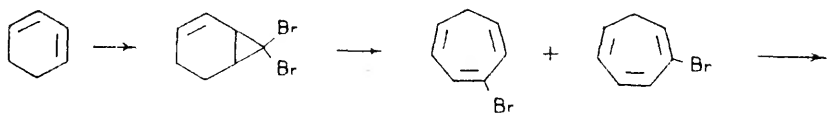
Chlorotropylium chloride was synthesized from tropone by reaction with oxalyl chloride in methylene chloride. This was reduced to the above mixture of chlorocycloheptatrienes with lithium aluminum hydride. Before an attempt was made to separate the isomers, the mixture was tested

with Simmons-Smith reagent to insure its reaction. Copper-zinc couple was prepared by the method of LeGoff¹⁷ and its reactivity with methylene iodide confirmed in the presence of cyclohexene. Repeated reaction of the reactive couple



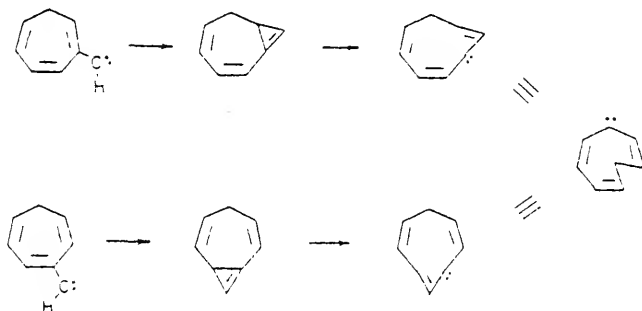
with methylene iodide in the presence of the chlorocycloheptatriene mixture resulted only in the recovery of the starting chlorides.

Attention was then diverted to preparation of 3 via



rearrangement of cycloheptatrienylcarbene. Lindsay and Reese¹⁸ have synthesized 2- and 3-bromocycloheptatriene by heating 7,7-dibromobicyclo[4.1.0]-2-heptene in quinoline. Dibromocarbene was generated from bromoform by reaction with potassium 5-butoxide in pentane, and allowed to react with 1,3-cyclohexadiene, yielding this bicyclic dibromide. This was heated in quinoline, under vacuum, distilling off the

mixture of bromides as they were formed. This mixture was then allowed to react with methyllithium in THF at -78° .

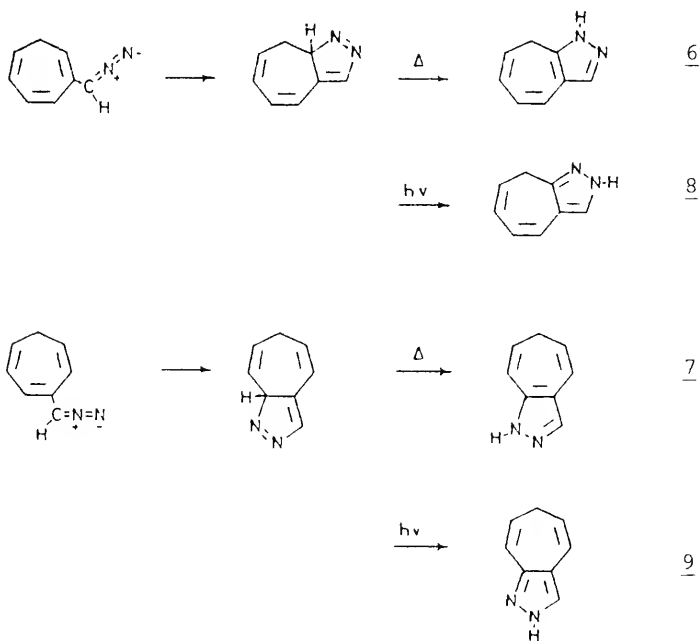


Addition of dimethylformamide to this lithium reagent at this temperature and hydrolysis with aqueous ammonium chloride yielded a mixture of 2-, and 3-formylcycloheptatrienes. The tosylhydrazones were generated from reaction of this mixture with tosylhydrazide in ethanol and the sodium salts by reaction with sodium hydride in THF.

It can be seen from the scheme above that isolation of pure isomers of these sodium salts is not necessary; both carbenes generated from these salts should yield the same homoaromatic carbene upon rearrangement.

This mixture of salts was thermally decomposed by refluxing in diglyme. The resulting material was taken up in water to dissolve the sodium toluenesulfinate formed and the aqueous phase was extracted with pentane. No products could be found in the pentane fraction. Extraction of the aqueous phase with ether yielded an oil containing two components. These were identified as $C_8H_8N_2$ isomers by high resolution mass spectrometry.

Assignment of the structures as pyrazoles 6 and 7 was accomplished by nmr. Two signals appeared in the region expected for resonances corresponding to the methylene protons. The triplet at 2.68* was assigned to the protons on C₄ of isomer 7 flanked by the protons on C₃ and C₅; while the doublet at 3.47 corresponded to the hydrogens on C₆ of isomer 6, adjacent to the proton on C₅. Two singlets at 7.5 and 7.6, corresponding to a single proton each, were assigned



to isomers 6 and 7, respectively, by comparison of the area of the integrated signals with those already assigned to the

*All proton shifts are reported in units of δ .

methylene protons. These were determined to be the protons on C_8 by comparison with the spectra of substituted pyrazoles.¹⁹ These protons, in other pyrazoles, center around 7.6. The vinyl signals could not be assigned to their particular isomers.

Formation of these pyrazoles is explained in the scheme above. Loss of sodium toluenesulfinate from the salt mixture yields the corresponding diazo compounds. These can then close to yield the indicated 3-H pyrazoles. Tautomerism via migration of the indicated proton yields 6 and 7 directly.

The formation of pyrazoles by this scheme is a well documented barrier to the formation of carbenes from tosylhydrazones. Bartlett and Stevens²⁰ have noted the tendency of diazo compounds generated from tosylhydrazones of α,β -unsaturated aldehydes to close in this way to yield the corresponding 3-H pyrazoles. While there seems to be no way to overcome this difficulty in the thermal decomposition of the sodium salts, low temperature photolysis²¹ has been utilized successfully in some cases to yield carbenes from systems that otherwise give only these pyrazoles.

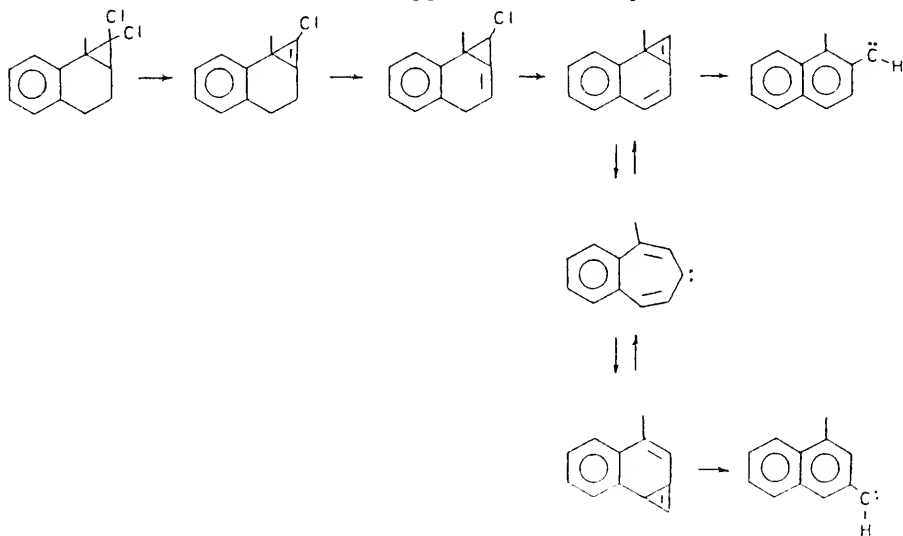
When our salts were photolyzed through Pyrex in THF and worked up in a manner similar to that described above, a mixture of two new compounds was isolated. Mass spectra of this material confirmed that these were also $C_8H_8N_2$ isomers. Again no evidence of compounds not containing nitrogen was seen.

These new pyrazoles, 8 and 9, were shown not to be the intermediate 3-H pyrazoles postulated above by the presence of a N-H stretch in the infrared at 3200 cm^{-1} . Neither did they rearrange to 6 and 7 by heating in refluxing diglyme. The nmr did show a superimposed doublet and triplet between 2.7 and 3.0 that appear to be the protons on the methylene carbons, and signals at 7.3 and 7.5 that appear to be the protons on C_8 . The other signals, again, could not be assigned to any isomer with any certainty.

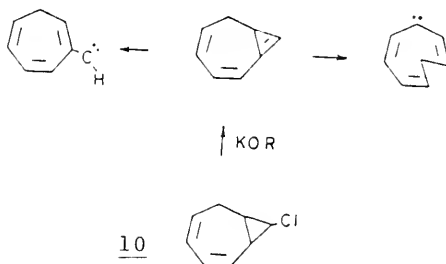
These pyrazoles might result from a photoinduced tautomerism of 6 and 7. Tautomerism of pyrazoles of this type is well known.²²

Attempts to alleviate the cyclization problem by low temperature photolysis failed.

Because of the difficulties involved in the low temperature photolysis, a new approach to the problem was taken.



Billups and Reed²³ has shown that it is possible to generate both carbene participants of a carbene-carbene rearrangement from the intermediate cyclopropene, formed by the dehydro-



halogenation of a di-halocyclopropane (vide supra).

This suggests the possibility that it might be possible to generate the homoaromatic carbene by dehydrohalogenation of an 8-halobicyclo[5.1.0]2,4-octadiene.

Synthesis of 10 was attempted by the addition of chloro-carbene to cycloheptatriene. This reaction yielded a yellow oil. Elemental analysis and high resolution mass spectrometry showed that this material was a $\text{C}_8\text{H}_9\text{Cl}$ isomer, as expected. The nmr implied the presence of two isomers. A multiplet at 1.3-1.8 was assigned to the two bridgehead protons and a multiplet centered at 2.5 was assigned to the methylene protons on C_6 . The vinyl protons were represented by a multiplet centered at 5.8. Two apparent triplets at 3.6 ($J = 3 \text{ Hz}$) and 3.0 ($J = 8 \text{ Hz}$) appeared in the area of the spectrum in which the proton on the carbon bearing the chlorine should lie.

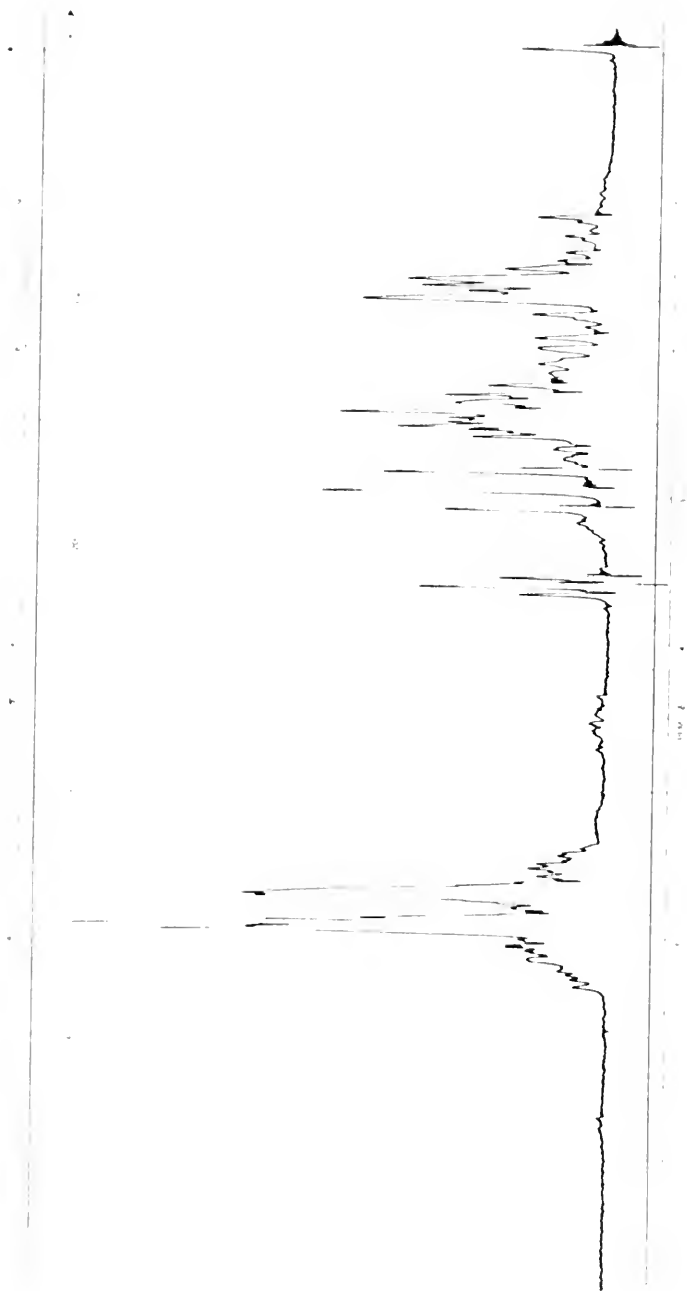
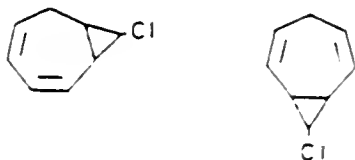


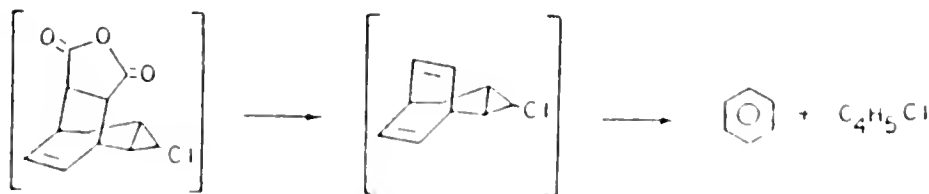
Figure 1. ^1H nmr Spectrum of cis- and trans-8-Chlorobicyclo[5.1.0]2,4-octadiene (10).

It was disturbing that the signals that correspond to the protons geminal to the chlorine in these compounds appeared to be triplets. Simple first order effects would lead to the conclusion that these protons would be represented as doublets of doublets if the carbene had inserted, as



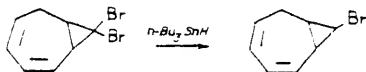
expected, into the 1,2 bond of the cycloheptatriene. If insertion had occurred into the 3,4 bond of the cycloheptatriene, the symmetry of the resulting chlorides would be expected to result in triplets corresponding to these protons.

Two proofs of structure for this molecule were attempted. If insertion of chlorocarbene in the 1,2 bond had occurred to yield 10, the resulting molecule would contain a conjugated diene. This diene would be capable of undergoing a Diels-Alder reaction with a dienophile. When the chloride was allowed to react with maleic anhydride, a solid material was isolated that was shown by mass spectrometry and nmr to be the expected adduct. Fragmentation of the molecule in the mass spectrometer was indicative of its structure. The molecular ion (m/e 238) lost CO and CO₂ to yield a new ion of mass 166. This fragmented to C₄H₅Cl⁺ and benzene (parent



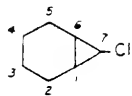
ion), implying the structure above. The nmr supported this structure and the infrared showed the expected anhydride doublet at 1775 and 1850 cm^{-1} .

Further support of 10 as the structure of this oil was obtained by synthesis of a model compound. The known isomer, 8,8-dibromobicyclo[5.1.0]2,4-octadiene, was synthesized by the method of Van Vooren et al.²⁴ This was allowed to react with freshly prepared tri-n-butyltin hydride,

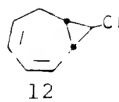
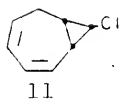


to yield a mixture of monobromides. The nmr of this mixture was identical to that of the mixture of chlorides.

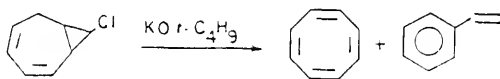
Closs et al.²⁵ have shown in studies of the 7-chlorobicyclo[4.1.0]heptane system that the coupling constant of the H_7 signal in the isomer, in which H_1 , H_6 , and the chlorine atom are cis, has a coupling constant of 3 Hz. From this information, the material isolated from the chlorocarbene reaction was assigned the structures 11 and 12. Isomer



11, in which the protons on the cyclopropane are assumed to be cis ($J = 8 \text{ Hz}$), is the major constituent, comprising 75% of the isomer mixture. This mixture could not be separated by chromatographic methods or spinning band distillation.



The mixture of 11 and 12 was subjected to five equivalents of potassium t-butoxide in THF at reflux. Work up with water and extraction into pentane yielded a small amount of cyclooctatetraene and styrene as the only isolable products. The cyclooctatetraene was determined not to rearrange to styrene under these conditions. The identity of these compounds was confirmed by the nmr spectra and comparison of their retention times to those of authentic samples upon gas chromatography. The balance of the material remained as an intractable polymer.



Because of the low yield of products from this reaction, an experiment was undertaken to determine if preferential reaction of one of the isomers in the mixture was taking place. To a solution of the above chlorides in THF at room temperature was added only a half equivalent of potassium t-butoxide. This was worked up with water and pentane to ultimately yield an oil containing cyclooctatetraene and a mixture of the above chlorides, heavily enriched (92%) in isomer 11. The cyclooctatetraene was removed by careful bulb to bulb distillation. This enriched mixture was then

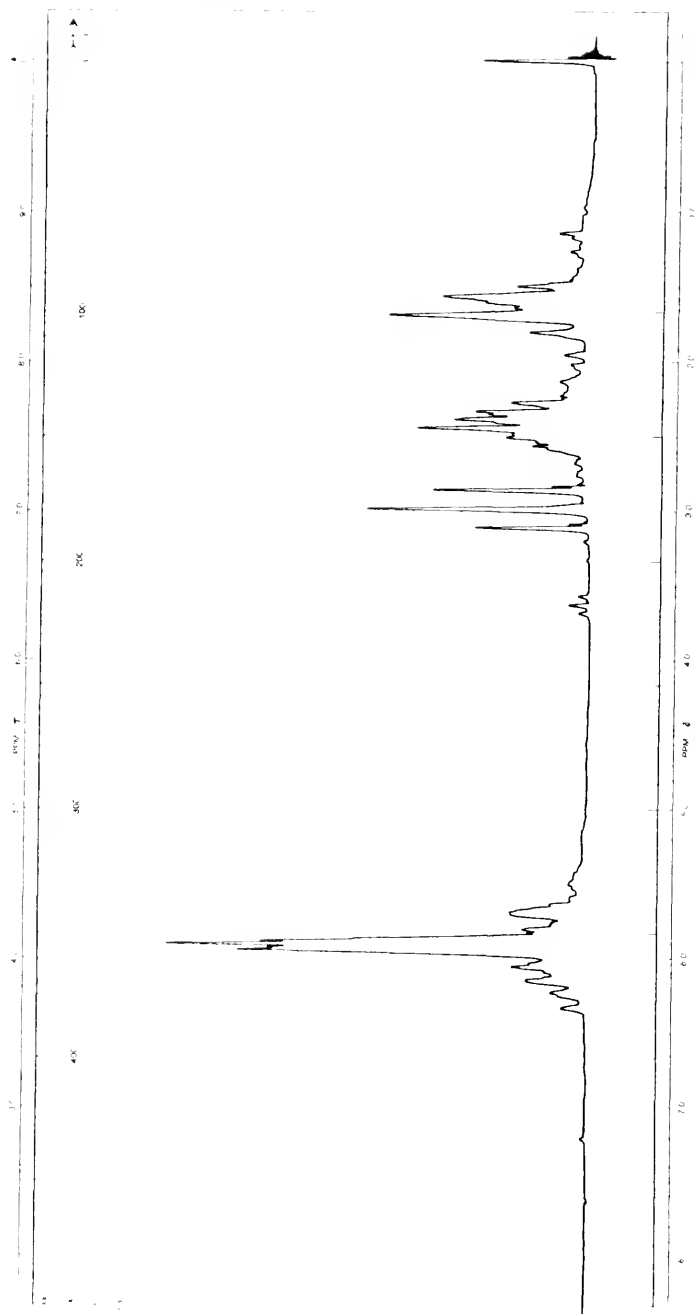
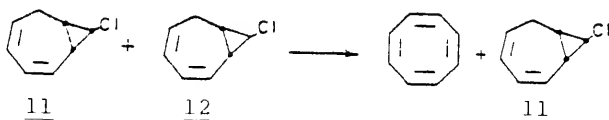


Figure 2. ^1H NMR Spectrum of cis- and trans-8-Chlorobicyclo[5.1.0]2,4-octadiene (10), Enriched in cis-8-Chlorobicyclo[5.1.0]2,4-octadiene (11).

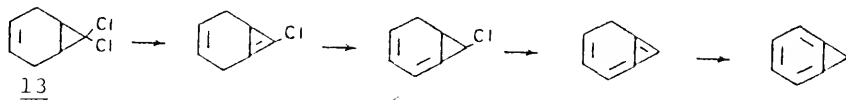
allowed to react with five equivalents of potassium t-butoxide in the original manner. Only a trace of cyclooctatetraene was found after work up, an amount that could easily be explained by reaction of the residual amount of 12 in the starting mixture. No residual 11 was isolated



from this reaction.

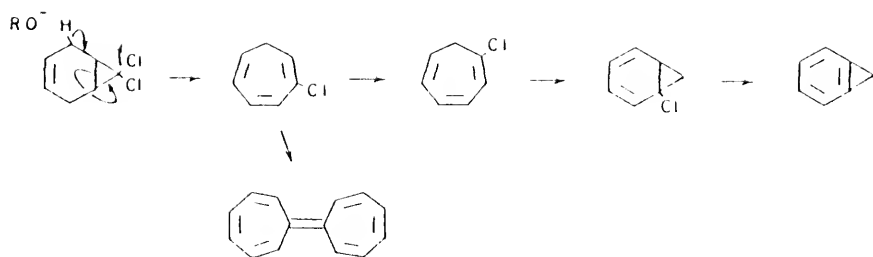
Attempts were made to trap either the cyclopropene or one of the possible carbenes formed in this reaction. No trapped products were seen using styrene, tetramethylethylene, t-butyl alcohol, butadiene or cyclopentadiene.

Cyclooctatetraene and styrene can be explained by a scheme similar to that derived by Billups²⁶ in his synthesis of benzocyclopropene. He has shown that 13, when allowed to react with potassium t-butoxide in DMSO, undergoes a dehydrohalogenation to the cyclopropene, which rearranges to the methylenecyclopropane moiety shown. Repetition of this

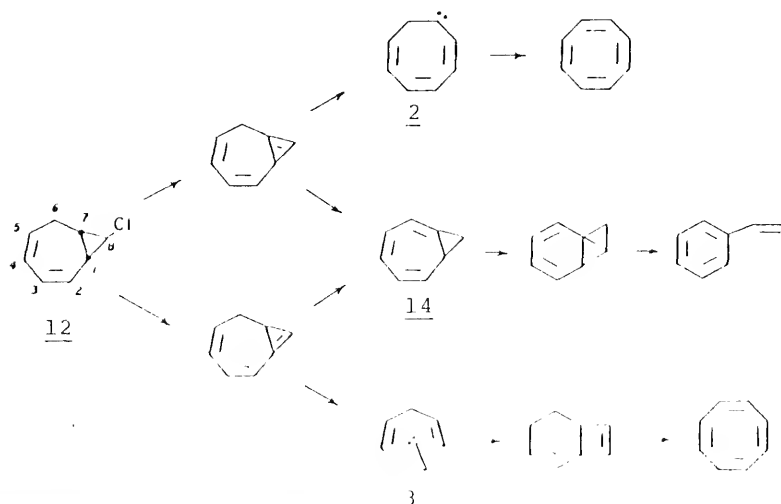


sequence yields benzocyclopropene.

A scheme in which an allyl hydrogen is removed by base, with concerted loss of chloride ion to yield an intermediate chlorocycloheptatriene has been discounted by labeling studies of Prestien and Gunther²⁷ and the absence of heptafulvalene,²⁸ which would have been formed under these conditions.



Loss of HCl in 12 can occur in one of two ways. If loss of the proton on C₇ occurs first, the resulting C₇-C₈ cyclopropene has the choice of two possible pathways. The homocycloheptatrienylidene, 2, would result from the ring expansion of the cyclopropene to the carbene. This carbene would be expected to rapidly rearrange to yield cyclooctatetraene. Base assisted isomerization of the cyclopropene to the methylenecyclopropane²⁹ yields the bicyclic triene, 14. This moiety can then undergo a norcaradiene rearrangement to the bicyclobutane shown. This, when it opens in its



usual manner, yields styrene.

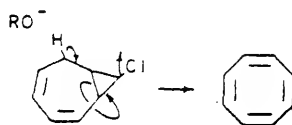
Loss of the hydrogen on C₁ to ultimately yield a C₁-C₈ cyclopropene, has the same options as the cyclopropene postulated above. Base assisted isomerization again yields 14 and ultimately styrene. This time, ring opening to the carbene yields homocycloheptatrienylidene, 3. This carbene does not possess the ability to migrate hydrogen as 2. However, it is apparent, upon study of molecular models, that the empty orbital of the carbene and the hydrogen on the methylene carbon are in excellent alignment for insertion of the carbene into this C-H bond. Intramolecular insertions of carbenes into carbon-hydrogen bonds in saturated and unsaturated rings are not only well known, but this reaction is competitive with possible 1,2 hydrogen migrations.³⁰ This insertion gives the bicyclic octatriene shown. This species is the well known valence isomer of cyclooctatetraene. Simple electrocyclic opening of the cyclobutene moiety results in cyclooctatetraene.

It is not unexpected that the above carbenes were not trapped by any olefin or alcohol. The inability to trap carbenes of this sort has become a generality.

With few exceptions, it can be stated that if a singlet carbene has an internal insertion or cycloaddition available, it will not be possible to trap it with an external reagent.³¹

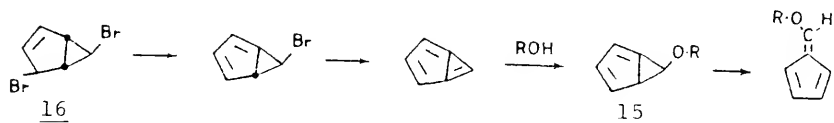
A direct opening of the chloride by reaction with the base appears extremely unlikely in light of the labeling studies in the benzocyclopropene system mentioned above.

However, in the case at hand, it is not possible, due to the unique symmetry of the cyclooctatetraene molecule, to carry out labeling studies of the type performed by Prestien and

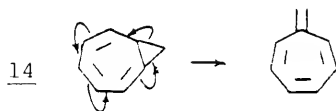


Gunther to disprove this pathway.

It is apparent from the low yield of cyclooctatetraene and styrene that some other route is available for reaction of the chloride. An interesting similarity exists in intermediate 14 and intermediate 15, below. Washburn et al.³² has studied the dehydrohalogenation of the dibromide, 16, and determined, by studies using labeled dibromides, that



the reaction proceeds via the route shown below. Rearrangement of 15 to 8-t-butoxyfulvene is a simple electrocyclic ring opening of the methylenecyclopropane. If 14 does open, or could be induced to open in an analogous manner, it would

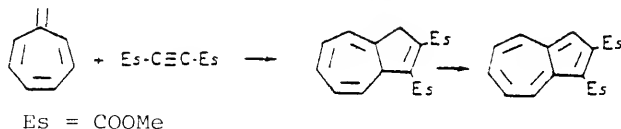


yield heptafulvene. This highly reactive material would polymerize rapidly under the reaction conditions.

An attempt was then made to induce reaction of the chlorides 11 and 12 to heptafulvene while minimizing destruction of any products formed. The reaction was carried out in a solution of potassium t-butoxide in tetraglyme, heated to 90° under vacuum to distill off volatile products into a liquid nitrogen cooled trap. Immediately upon injection of some of the mixture of chlorides into this solution via syringe, a scarlet material was noted in the liquid nitrogen trap. Upon warming, the scarlet material polymerized. Gas chromatography showed the presence of cyclooctatetraene and styrene in the trapped material.

An attempt was then made to trap this material by the method of Doering and Wiley.³³ The above reaction was repeated, and the contents of the cold trap were washed into cold THF containing dimethyl acetylenedicarboxylate. After standing at 0° for 72 hours, the red color had disappeared. Exchange of the solvent with benzene and air oxidation using Pd/C catalyst yielded a blue solid. This was identified, by comparison of its uv with the literature,³³ as dimethyl azulene-1,2-dicarboxylate.

When the red material was trapped in an nmr tube



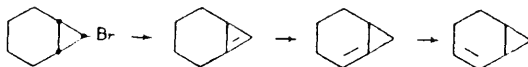
containing THF and a trace of triethylamine, an nmr was taken that showed signals corresponding to those reported for heptafulvene.³⁴

When this reaction was repeated with pure 11 under the same conditions, a very small amount of colored material was obtained, not enough to identify by the methods outlined above.

It is obvious from the preceding reactions that only one isomer, 12, is yielding isolable products. Preferential reaction of this isomer in which the hydrogen and chloride to be eliminated are coplanar might be expected. It is unusual that reaction of isomer 11 does occur, albeit slowly, but does not give the same products.

No evidence can be found in the literature on the relative rates of elimination between the isomers of monohalocyclopropanes. While the number of reactions is small,³⁵ one set of experiments has shown that elimination, when the hydrogen vicinal to the halide is trans, can occur and yields the cyclopropene.³⁶ The reaction pathway of isomer 11 cannot be suggested, since the only material isolated from its addition to base is an intractable polymer.

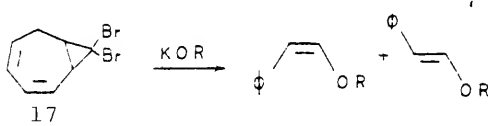
In order to increase the yield so that the reaction



could be more readily studied, a system was then sought in which the configuration of the eliminated moieties could be assured to be cis. The simplest system of this kind would be an 8,8-dibromobicyclo[5.1.0]2,4-octadiene, 17. In this molecule, one of the halogens will always be cis to the hydrogen to be eliminated.

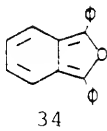
When this molecule was subjected to potassium t-butoxide in THF at 0° and worked up with water and pentane as outlined above, a very small amount of two compounds could be isolated. These were separated by TLC and their structures identified as cis and trans-β-t-butoxystyrene by nmr and mass spectrometry. No bromocyclooctatetraene was noted in this reaction.

Since the mechanisms of these reactions were merely



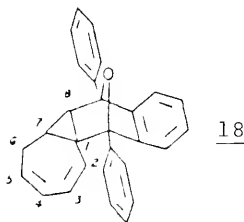
speculative at this time, it was then set about to confirm intermediates along these suspected pathways. The first intermediate, one common to both systems, is the cyclopropene formed from the initial dehydrohalogenation.

The first attempt was made to trap this cyclopropene by a Diels-Alder addition to 1,3-diphenylisobenzofuran, 34.³⁷ It has been shown that 34 is a potent diene in Diels-Alder reactions. Its large molecular weight would make isolation of the trapped material possible by crystallization.



The mixture of chlorides, 11 and 12 (1 equivalent of 12), was allowed to react with five equivalents of potassium

t-butoxide and one equivalent of 34 at -78° in THF. Along with some cyclooctatetraene and a great deal of 11, a crystalline material was isolated after work up with ether. Chromatography and recrystallization allowed isolation of the crystalline material which was identified as the 34 adduct of the cyclopropene, 18. Elemental analysis and high resolution mass spectrometry confirm the $C_{28}H_{22}O$ formula. The proton spectrum showed the expected shifts for this molecule, a complex multiplet for the aromatics from 7.0-8.0 (14H), a vinyl multiplet at 5.8-6.2 (4H), a doublet at 1.7 (1H) and a complex multiplet from 2.1-3.2 that corresponds to three protons. Confirmation of the exact structure could not be made from this spectrum alone. As mentioned above, dehydrohalogenation could occur across either C_1-C_8 or C_7-C_8 to yield the cyclopropenes below. Either of these materials,



when trapped with 34, could give signals of this type in the proton spectrum. The complex coupling precluded a simple assignment of structure.

Spin decoupling allowed the assignment of this molecule as structure 18 to be carried out. The complex multiplet from 2.1 to 3.2 was suspected to be formed from the signals

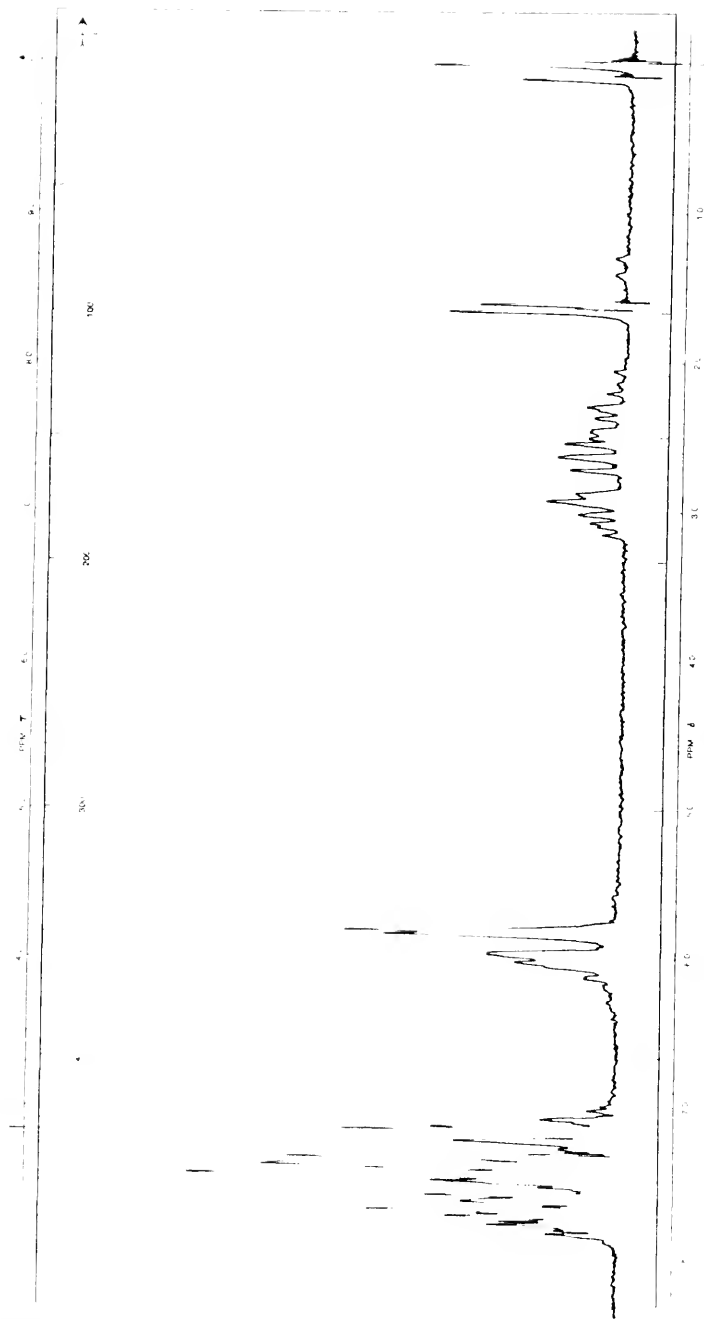
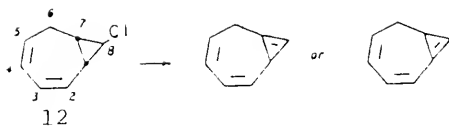


Figure 3. ^1H nmr Spectrum of the 1,3-Diphenylisobenzofuran Adduct of 2,4,8-Bicyclo-[5.1.0]octatriene (18).



of the methylene protons (H_6) and the bridgehead proton (H_7). When the doublet at 1.7, assigned to H_8 , was irradiated, the far downfield portion of the multiplet simplified to a doublet of doublets ($J=4.5, 9$ Hz.). This would denote that this proton (H_7) while being adjacent to H_8 , was also being split by two non equivalent protons ($H_{6a,b}$). Irradiation of the downfield portion of the vinyl signal (H_5) resulted in two overlapping doublets of doublets ($J=4.5, 14$ Hz.; $8.5, 14$ Hz.) in the upfield portion of the 2.1-3.2 multiplet. These two non equivalent protons ($H_{6a,b}$) were being split, not only by an adjacent proton (H_7), but also by each other. This is the reason for the identical coupling constant ($J=14$ Hz.) in each of these patterns. This type of coupling cannot be explained by a product resulting from the addition of 34 to the C_7-C_8 cyclopropene.

Similar reaction of 8,8-dichlorobicyclo[5.1.0]2,4-octadiene with five equivalents of potassium *t*-butoxide and *i*BF results in a crystalline material after the same type of work up. An almost identical material is isolated from the reaction of 17 in a similar manner. Each of these compounds is a $C_{28}H_{21}OX$ isomer with almost identical proton spectra.

These isomers were assigned structures 19 and 20. The molecular formulas were confirmed by elemental analyses.

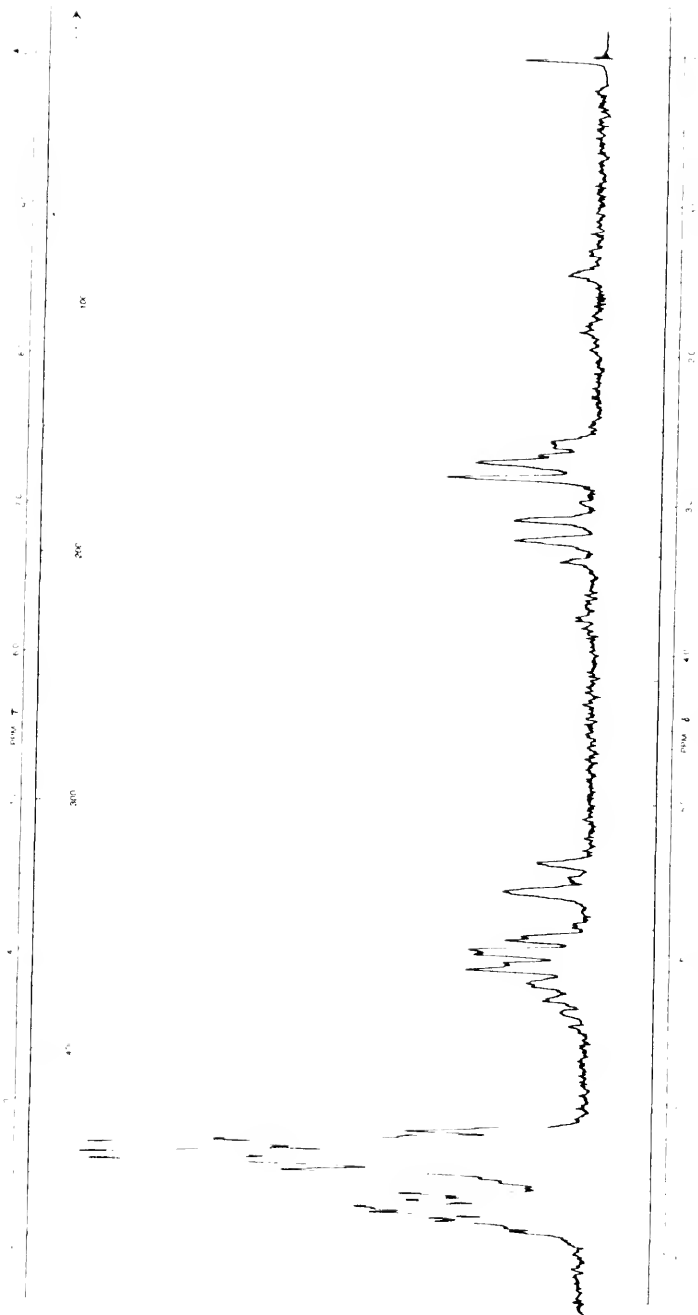
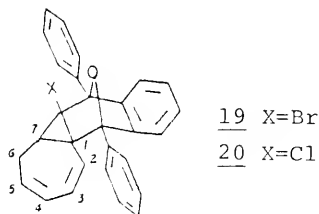


Figure 4. ^1H nmr Spectrum of the 1,3-Diphenylisobenzofuran Adduct of 8-Bromobicyclo-[5.1.0]2,4,8-octatriene (19).

The proton spectrum of the bromide, 19, as in the case of 18, could not unequivocally establish the structure. Each of the protons could be assigned to a signal but the splitting was not simple enough to define the structure exactly. A two proton multiplet centered at 2.6 was assigned to the methylene protons on C₆ and a multiplet at 3.2 was assigned to H₇, each of these signals appearing at a similar shift to the

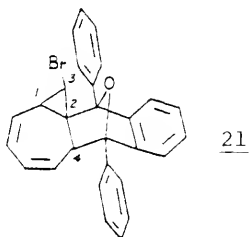


corresponding protons on 18. The aromatics again appear in a multiplet from 5.9-6.5. A glaring deviation from the vinyl signals of 18 existed in the appearance of a new doublet at 5.5. This signal could be assigned to H₂. A more complete discussion will appear later.

The ability to work with a greater amount of the reactive isomer (vide supra) in the dibromide system, resulting in a greater yield of trapped material, allowed studies of the carbon-13 spectrum. The distinct dissimilarity of the proton vinyl signals raised a real question as to the similarity of structures assigned to this bromide and the hydrocarbon, 18. The absence of bromocyclooctatetraene in any reaction of the dibromide, 17, with base suggests that rearrangement of the cyclopropene to the methylenecyclopro-

pane must be a rapid reaction. If this is true, then this trapped bromide might be formed from the methylenecyclopropane rather than the cyclopropene.

The bromide expected from the trapping of a methylenecyclopropane with 34 would be 21. This could be easily differentiated from the trapped cyclopropene by the fact that this molecule contains three methyne carbons (C_1 , C_3 , C_4) and one quaternary carbon in what would be expected to be the up-field portion of the carbon-13 spectrum. Structure 19 con-



tains one methylene carbon (C_6), one methyne carbon (C_7), and two quaternary carbons (C_1 , C_8) in the corresponding portion of the carbon spectrum. The carbon-13 spectrum of this bromide showed a triplet at 27.873 (ppm downfield from tms), a doublet at 35.401 and two singlets at 41.372 and 48.461. The triplet was assigned to the methylene carbon (C_6) on 19, the doublet to the methyne carbon (C_7) and the singlets to the quaternary carbons (C_1 , C_8).

Final confirming evidence for 19 as the structure of this solid was found in the spin decoupled proton spectrum. When the signal at 2.6 (H_6) was irradiated, the vinyl multiplet split into a doublet and a triplet, denoting that the

protons on C_6 are the only protons adjacent to the vinyl system.

The dissimilarity in the vinyl signals of the proton spectra of 18 and 19 can be explained when models of these two systems are constructed. In structure 18, there are two conformations with respect to ring flip of the seven-membered ring. In one of these conformations, one of the protons on C_6 is almost coplanar with H_8 . In this conformation, the proton on C_2 is removed from the proximity of the neighboring phenyl ring, eliminating any steric interaction. When the same conformation is attempted in compound 19, the proton on C_6 is now almost coplanar with the bromine. Indeed, this exact conformation cannot exist because of the steric bulk of this halide. A ring flip to the other conformation eliminates this steric problem, but in doing so, forces the proton on C_2 into the shielding area of the neighboring phenyl ring. This, in turn, shifts this proton signal upfield, generating the doublet at 5.5 that was noted in the spectrum of 18.

The next step, following the proposed mechanism, would be to trap the methylene cyclopropane, if possible. This was attempted in the dibromide system because of the aforementioned reactivity of this material. At 0° , one equivalent of 17 was allowed to react with five equivalents of potassium t-butoxide and one equivalent of 34. Again a crystalline material was isolated in the same manner as before. The structure of this material was determined to be

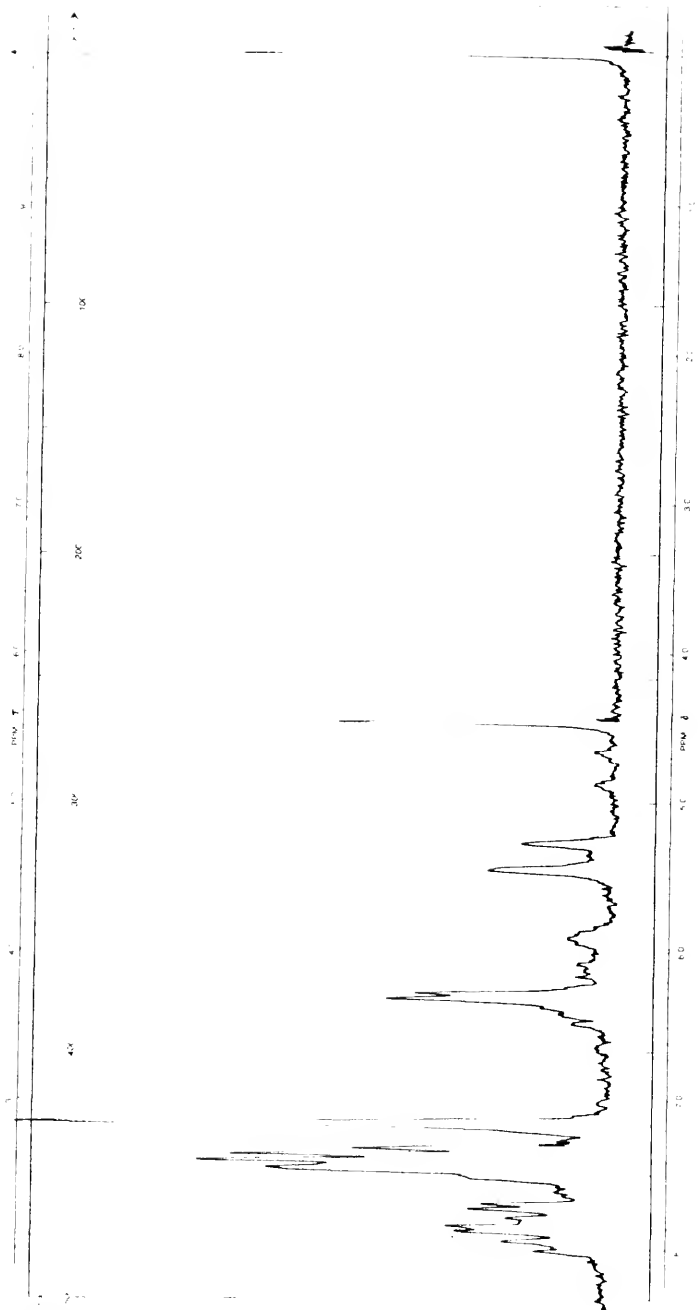
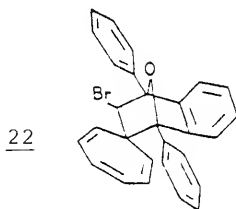


Figure 5. ^1H nmr Spectrum of the 1,3-Diphenylisobenzofuran Adduct of 8-Bromohptafulvene (22).

22. High resolution mass spectrometry confirmed a $C_{28}H_{21}OBr$ formula. The proton spectrum showed no upfield protons, implying that the cyclopropane ring had been broken. The vinyl signals consisted of a six proton multiplet between 5.2-6.5, the aromatics, a fourteen proton multiplet between 7.1-8.0 and the remaining signal was a singlet, corresponding to one proton at 4.5.

The carbon-13 spectrum supported this structure. The upfield portion of this spectrum indicated four sp^3 carbons. Two of these signals could be assigned to the bridgehead carbons of bicyclic ether by their similarity to the respective carbons in structure 19. The only sp^3 signal that de-



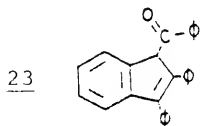
noted a proton bearing carbon was a doublet at 66.101 that was assigned to C_1 . The remaining quaternary signal (56.898) was assigned to C_2 .

This molecule is a labile material and readily aromatizes with loss of HBr to yield a more stable new material. This material, a $C_{28}H_{20}O$ isomer, 23, is isolated after chromatography on silica gel of the crude material from the reaction of 17 with potassium t-butoxide and 34 at 0° , although it cannot be detected in the nmr of the crude material before chromatography. This halogen-free substance

is the only material isolated from a solution of 22 in acetonitrile allowed to stand at room temperature for two days.

Spectral data allowed structure 23 to be assigned. Elemental analysis and high resolution mass spectrometry confirm the $C_{28}H_{20}O$ formula. The infrared spectrum indicated a carbonyl stretch at 1670 cm^{-1} , corroborated by a large loss of $\text{Ph-Co}(+)$ from the molecular ion in the mass spectrum. The proton spectrum was simple, containing a multiplet between 6.9 and 7.7, implying a high degree of aromatization and no indication of protons on vinyl positions. The only other proton signal was a singlet at 5.5 corresponding to one proton. The only assignable signals in the carbon-13 spectrum were the carbonyl carbon at 198.97 and a proton bearing carbon at 63.44.

These data can be fit to a 1,2,3 trisubstituted indene in which the substituents are two phenyls and a benzoyl. Synthesis of 1-carbomethoxy-2,3-diphenylindene has been reported³⁸ and the proton on C_1 is a singlet at 4.8. This molecule was used as a basis for calculation of chemical shifts by the additivity rules of Shoolery.³⁹ The additivity factor was taken as the difference in the shifts of the



methyl signals of acetophenone and methyl acetate (+.6 ppm). Using this information, the calculated shift for this proton in 1-benzoyl-2,3-diphenylindene would be 5.4.

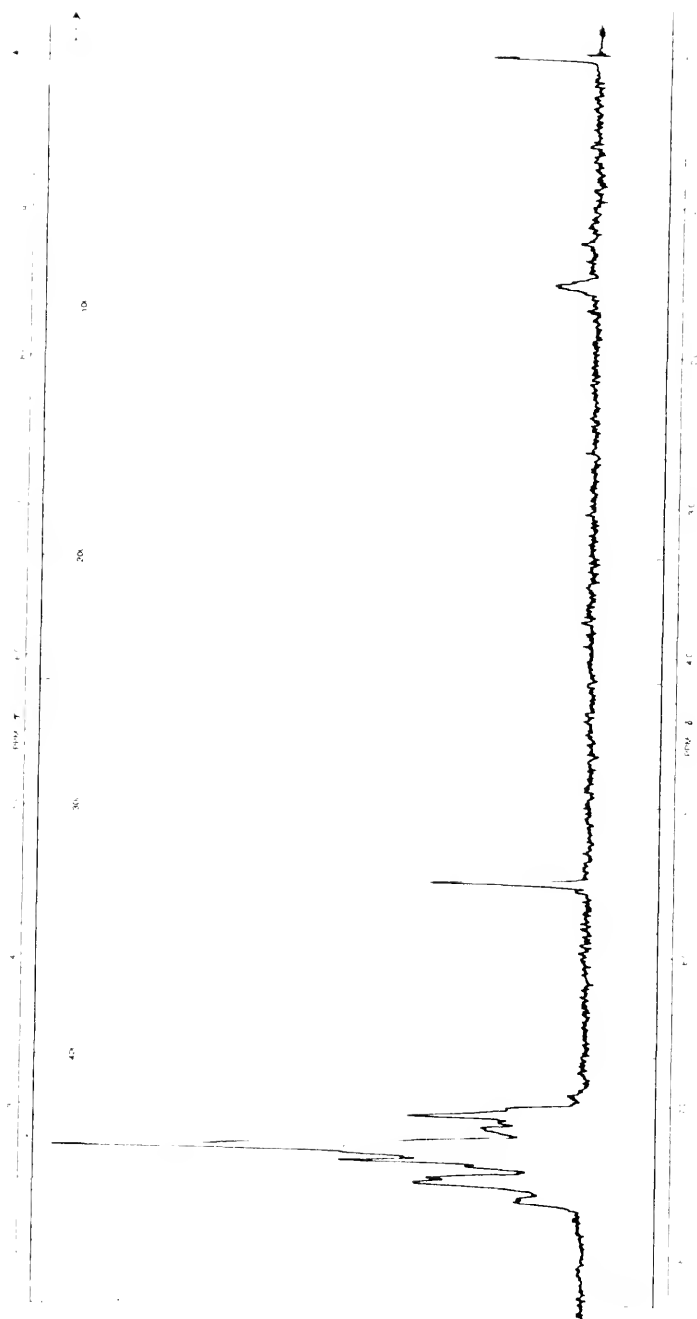
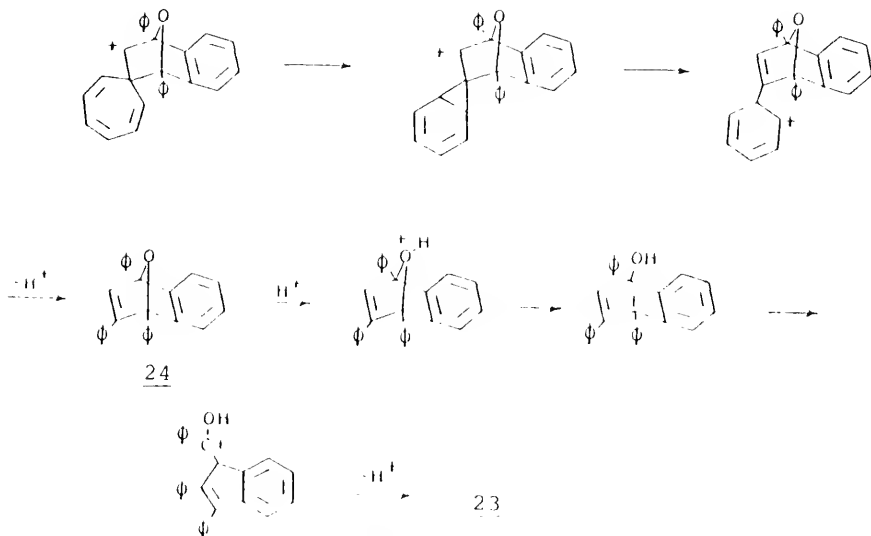


Figure 6. ^1H nmr Spectrum of 1-Benzoyl-2,3-diphenylindene (23).

The isolation of 23 from 22 in acetonitrile shows that a solvolytic dehydrohalogenation is one possible mechanism. Loss of the bromide would yield the carbonium ion below. Isomerization of the cycloheptatriene ring to a norcaradiene yields a cyclopropylcarbiny cation. Interconversion of this carbon to the allylcarbiny cation results in a species that can lose a proton to aromatize. This new compound, 24, could protonate on the oxygen and rearrange, as outlined below, to 23.

Compound 24 should be stable in the absence of acid. If solvolysis of 22 occurs under the basic conditions of the reaction in which 22 is generated, 24 may be an isolable product.

Benzynes was allowed to react with 2,3,5-triphenylfuran⁴⁰ to yield a colorless solid whose nmr and mass spectra are compatible with the structure of 24. The proton spectrum of



this material consists of a multiplet between 6.9-7.9. The carbon spectrum shows the bridgehead carbons (92.416 and 94.950) at positions comparable with those on 19 and 22. The rest of the spectrum cannot be assigned.

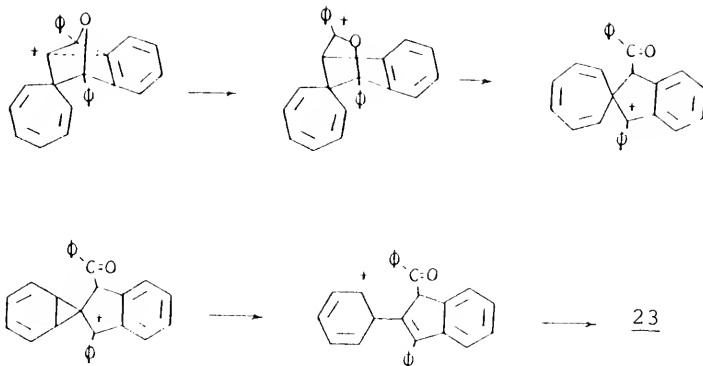
The intermediacy of this material in the solvolysis of 22 was refuted by its stability to silica gel chromatography and its inertness in acetonitrile solution. Refluxing this material in acidic methanol produced no 23.

With this in mind, it is more likely that the actual mechanism of the solvolysis of 22 resembles that below. Loss of bromide ion yields a non classical carbonium ion that

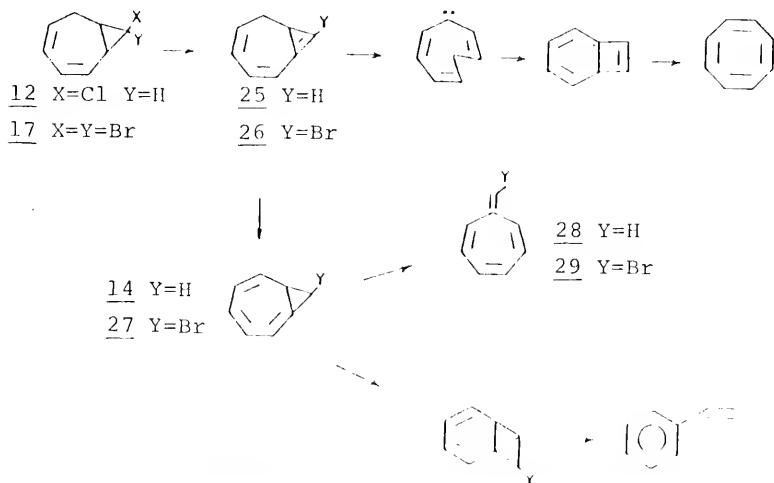


opens, as indicated, and rearranges to the ketone. The cyclopropylcarbinyl cation formed from rearrangement of the cycloheptatriene to norcaradiene, rearranges to the allyl-carbinyl cation, which aromatizes to 23.

Dehydrohalogenation in the systems of 12 and 17 seem to follow a similar pathway. The first step is dehydrohalogenation across the C_1 - C_8 bond to yield the cyclopropene. This, in the case of the halogen free cyclopropene, 25, has the ability to open to the homoaromatic carbene 3, which can intramolecularly insert into the C-H bond of the methylene across the ring to form the bicyclic triene, which can then open to cyclooctatetraene. Competing with this reaction is



the base induced isomerization of the cyclopropene to the methylenecyclopropane. This moiety can apparently undergo electrocyclic ring opening to yield a heptafulvene. Both of these heptafulvenes have been trapped, 28 with the acetylene diester yielding the substituted azulene, and 29 with iBF to yield 22. The styrene formed in the reaction of 12 with base in the absence of trapping material appears to arise from a bicyclobutane formed by norcaradiene rearrangement



of 14. This would be consistent with the increase in yield of styrene noted by increasing the temperature of the reaction.

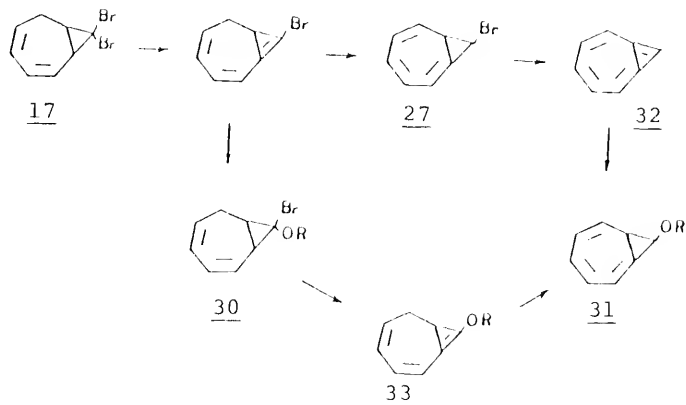
The absence of bromocyclooctatetraene in the reaction of 17 with base must be recalled. It is unlikely that the difference in the eliminated halide is changing the course of the reaction, since trapping of the halocyclopropene was accomplished regardless of the halide eliminated. The difference in these reactions is most likely caused by the rate at which the cyclopropene isomerizes to the methylenecyclopropane. The intermediate anion in this isomerization can be stabilized by resonance through the pi system and onto the carbon bearing the halide. The halogen can stabilize the anion at this position by induction. The overall effect is to enhance the ability of the cyclopropene to isomerize through this intermediate. This allows the cyclopropene to isomerize before opening to the carbene can occur.

The question of the genesis of the styrene ethers has still not been addressed. These ethers are only apparent in the reaction of 17 with no trapping material. At no time during the isolation of 19 or 22 were either of these compounds noted. It is apparent that to isolate these compounds, neglecting nucleophilic substitution of the t-butoxy group



for bromide, that two dehydrohalogenations must have occurred. Two plausible mechanistic pathways can be postulated.

The cyclopropane previously shown to have been found in this reaction can either be trapped with *t*-butyl alcohol to yield 30 or rearrange to 27. A second dehydrohalogenation of 30 with accompanying rearrangement to the methylenecyclopropane yields 31. This intermediate can also be formed from a dehydrohalogenation of 27 to yield the tetraene, 32, which can be trapped by *t*-butyl alcohol in a manner reminiscent of that of the trapping of *m*-benzynes to yield 15. Compound 31 can then aromatize, in the manner postulated earlier for the formation of styrene from the monochloride



system, to yield the styrene ethers.

To trap the progenitor of the ethers would require delay of inclusion of the trapping material until the bromocyclopropane could react further and the second dehydrohalogenation to either 32 or 33 could occur. The reaction must

be done at a low temperature to prevent the ring opening to bromoheptafulvalene known to occur at 0°.

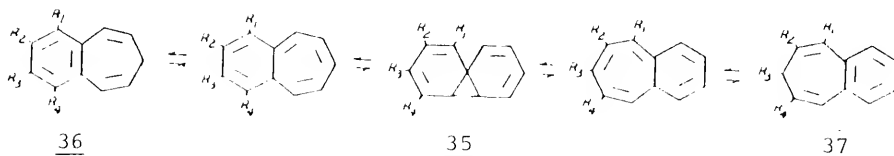
At -78°, the dibromide 17 and five equivalents of potassium 5-butoxide were stirred for one hour, then, while still at this temperature, one equivalent of 34 was introduced. When the reaction had warmed and was worked up with water and ether in the usual way, a large amount of polymer was noted. The only isolable product was a small amount of 22.

It is apparent that trapping of the doubly dehydrohalogenated material is not taking place. This is unfortunate in that identification of this material, which must be a precursor of the styrene ethers, cannot be made.

AN ATTEMPT TO GENERATE BISNORCARADIENE

Introduction

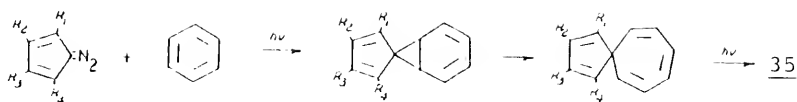
Bisnorcaradienes, 2,4,8,10-tricyclo[5.4.0.0^{1,6}]undecatetraenes, 35, have been postulated as intermediates to explain the scrambling of substituents in substituted benzocycloheptatrienes. These interesting intermediates were first postulated in the thermal isomerization of di-deutero-3,4-benzocycloheptatetraene by Gruber and Pomerantz,⁴¹ where it was noted that deuterium substituted on the cyclohepta-



triene ring of 3,4-benzocycloheptatriene (37; $R_1, R_3 = D$; $R_2, R_4 = H$) would rearrange to the benzene portion upon heating at 405° for 10 min. They postulated that the reaction proceeded through the scheme above.

The next system thought to involve bisnorcaradienes was that of Durr et al.⁴² in which a cyclopentadienylidene was allowed to react with benzene to ultimately yield a spiro compound that was thought to rearrange to the bisnorcaradiene by photolysis.

This photolytic reaction of the spiro compound was thought to proceed through the di- π -methane rearrangement to yield the bisnorcaradiene directly.

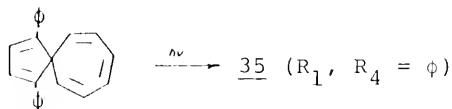


In 1974, Durr et al.⁴³ were able to isolate a material from the photolysis of the spiro compound, below, at -70° . This material was identified by its nmr at -60° as the

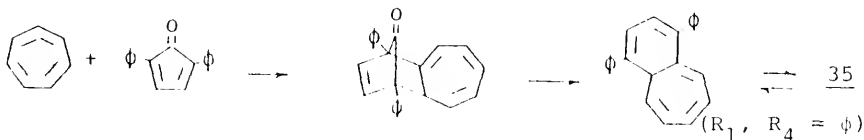


bisnorcaradiene. When this material was warmed to -10° , it isomerized to the benzocycloheptatrienes.

Also during that year, Mitsuhashi and Jones⁴⁴ isolated substituted benzocycloheptatrienes that were postulated to have been formed via an intermediate bisnorcaradiene, from the addition of cycloheptatrienyldiene to tetracyclones.

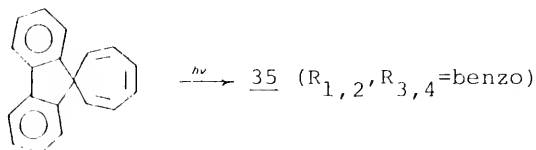


In 1976, Pauly and Durr⁴⁵ reported the isolation of a material that he identified by proton nmr as the first stable bisnorcaradiene.⁴⁶ This material, which melts at 104° , has a nmr spectrum similar to that of the material⁴⁶ isolated in the low temperature work mentioned above.



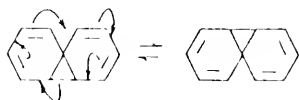
A possible property of this intermediate that has not been explored is the potential of 35 to undergo a degenerate [5,5] antara, antara, sigmatropic rearrangement. This reaction would be a symmetry allowed, concerted reaction.

It was with this possibility in mind that the system

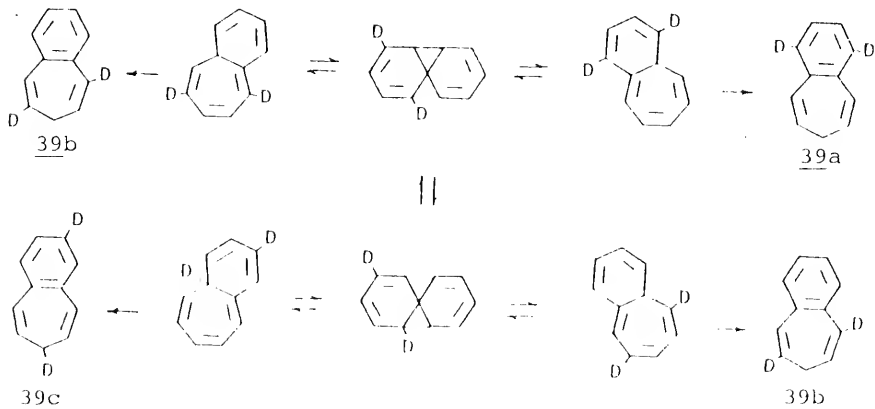


outlined below was devised.⁴⁷

This system would allow studies to be made of the possibility of bisnorcaradiene formation in the parent system at modest temperatures, and determination of the



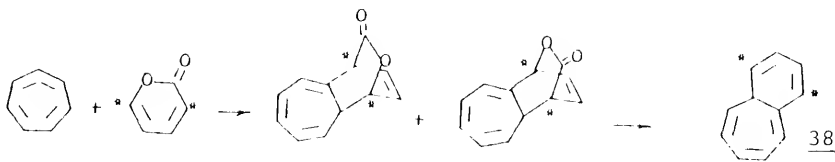
ability of this bisnorcaradiene to undergo this degenerate, semibulvalene type of rearrangement. The known first order



proton spectrum of 3,4-benzocycloheptatriene would allow simple assignment of the positions of the deuterium atoms in the rearranged molecules.

Entrance to this system would be made through compound 38. This 1,3,5,8,10-bicyclo[5.4.0]undecapentaene would have the potential to rearrange to bisnorcaradiene in the manner of the substituted analogues noted above. Compound 38 could be formed by the addition of cycloheptatrienyldiene-cycloheptatetraene to 3,6-di-deutero-2-pyrone. The resulting lactones could be decarboxylated to yield 38.

If the bisnorcaradiene were formed in this system, the resulting benzocycloheptatrienes should show deuterium in the cycloheptatriene ring (39a,39b). This effect would be evident in the changes in the splitting patterns of the vicinal hydrogens. If the [5,5] rearrangement should take

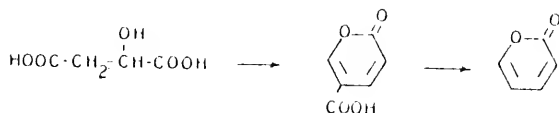


place, a new splitting pattern for H_1-H_6 should become evident due to the introduction of a new molecule with deuterium at C_7 (39).

Results and Discussion

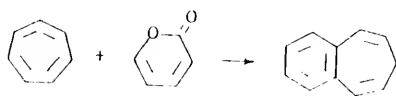
Coumalic acid, prepared by the method of Wiley and Smith⁴⁸ from malic acid, was decarboxylated at 650° through copper turnings to yield 2-pyrone.⁴⁹

Attempts to react 2-pyrone with cycloheptatetraene generated from chlorocycloheptatrienes and potassium *t*-butoxide⁵⁰ were unsuccessful due to the instability of the 2-pyrone in base. The 2-pyrone was reactive to cyclohep-



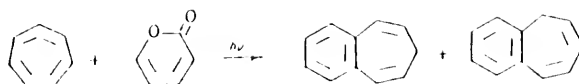
tetraene generated from the thermolysis of the sodium salt of tropone tosylhydrazone.⁵¹ When this salt was added to a solution of ten equivalents of 2-pyrone in diglyme at 110°, 3,4-benzocycloheptatriene was isolated, after work up with water and pentane, in 30% yield.

Similar results were seen after photolysis of the sodium salt through Pyrex in THF in the presence of ten equivalents of 2-pyrone. Again, 3,4-benzocycloheptatriene was isolated as the major component, but 1,2-benzocyclo-



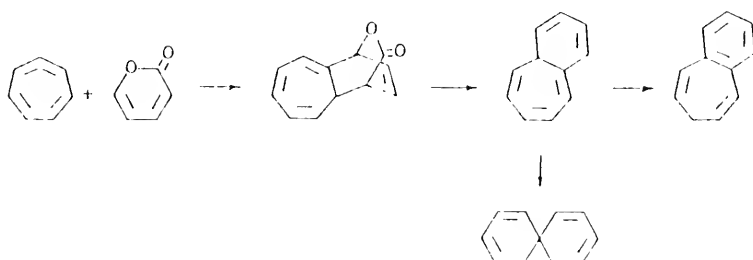
heptatriene was also formed. These results were noted in photolyses at temperatures as low as -78°. Photolyses were not as clean as the thermolyses, and polymeric materials were also isolated.

The mechanism of this reaction should be that proposed above, addition of the allene to the pyrone to yield the lactone and decarboxylation to the bicyclic pentaene.

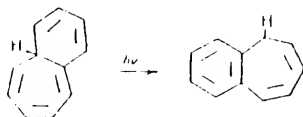


Hydrogen can migrate to yield the benzocycloheptatriene, or the ring can close to the bisnorcaradiene.

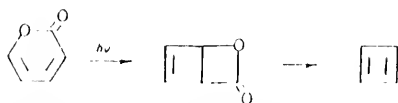
The presence of the 1,2-benzocycloheptatriene apparently results from a photoinitiated 1,3 hydrogen shift in the bicyclic pentaene.



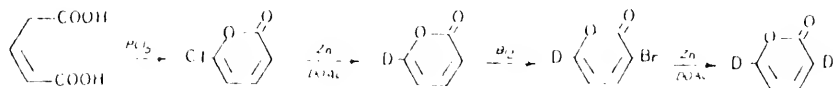
It was necessary to use an excess of 2-pyrone in the photolysis reaction because of the photolability of this molecule.⁵² It can undergo [2+2] cycloaddition intramolecu-



larly to yield a lactone that decarboxylates to cyclobutadiene.



Chapman et al.⁵² have been able to synthesize di-deutero-2-pyrones by sequential deuteration of the pyrone, from methods developed by Pirkle and Dines.⁵³



Synthesis of 6-d-2-pyrone, 40 was accomplished from glutaconic acid by the method shown above. Before the second deuteration was attempted, this material was allowed to react with cycloheptatetraene to determine if rearrangement through a bisnorcaradiene was taking place. Formation of the bisnorcaradiene would cause some of the deuterium to become incorporated into the cycloheptatriene portion of the product, after rearrangement.

Reaction of an equivalent amount of sodium salt with 40 in diglyme at 110° yielded the benzocycloheptatriene, as expected. There was no change in the splitting patterns of the proton spectrum, although the mass spectrum showed that the deuterium had been retained. Integration of the proton spectrum indicated that all of the deuterium was incorporated in the benzene portion.

This implied that the 1,5 hydrogen migration, resulting in the aromatization of the pentaene was much faster than the closure to a bisnorcaradiene. Since this migration is thermally initiated, an attempt was made to generate the cycloheptatetraene by photolysis of the sodium salt at -78°, as before. The scarcity of the deuterated pyrone precluded

the ability to work with the excess of starting material enjoyed in the reaction of the non-deuterated pyrone. Photolysis of an equivalent amount of the sodium salt and 40 at -78° did not yield enough benzocycloheptatriene to identify. No pyrone was recovered after the reaction.

An attempt was then made to determine if the closure to bisnorcaradiene could become competitive with aromatization by increasing the temperature of the reaction. At temperatures as high as 200° , aromatization remained as the only observable pathway of the pentaene.

It appears that the energy required to drive the pentaene toward aromatization and the energy required for closure to a bisnorcaradiene must not differ greatly. The effect of aryl substitution in this system is apparently enough to induce bisnorcaradiene formation by either retardation of aromatization or acceleration of closure. The nature of this is not obvious.

EXPERIMENTAL

General. All melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra (60 MHz) were recorded on either a Varian A-60A or JEOL PMX 60 spectrometer and are reported in ppm (δ) downfield from tetramethylsilane, the internal standard. Carbon-13 and 100 MHz proton spectra were recorded on a JEOL FX 100 spectrometer and are reported in ppm downfield from tetramethylsilane. Infrared data were recorded on a Beckman IR 10 spectrophotometer. Combustion analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Mass spectra were obtained on an AEI MS 30 spectrometer.

Cycloheptatriene was purified by distillation through a column of glass beads. All tetrahydrofuran (THF) was distilled from lithium aluminum hydride immediately before use. Diglyme and tetraglyme were distilled from calcium hydride and stored over sieves until used. Dimethylformamide (DMF) was stirred for 24 hrs over 3A molecular sieves and calcium hydride, decanted onto barium oxide and distilled at 20 mm into septum bottles containing molecular sieves. Other commercially obtained reagents were used as received.

Chromatography was carried out on Baker 60-200 mesh silica gel or Fisher basic alumina. The progress of column chromatography was followed by the addition of 1% type

609 phosphor (DuPont Photoproducts Department) to the adsorbent, employing a quartz column, and observing with a hand-held UV unit (Fisher Scientific).

Materials noted as vacuum dried were placed in a vacuum oven at 130° for at least 12 hours.

Preparation of tropone. In a 2 liter round-bottomed Morton Flask equipped with a mechanical stirrer and a reflux condenser was stirred 13.5 g (0.10 mol) of KH_2PO_4 in 33 ml of water and 350 ml of dioxane. To this was added in one portion, 46 g (0.50 mole) cycloheptatriene and 54 g (0.49 mol) of selenium dioxide. This suspension was then heated to 90° in an oil bath and stirred for 16 hours. After the mixture had cooled to room temperature, the residual selenium was filtered and the supernatant liquid added to 700 ml of water. This was then extracted four times with 250 ml of methylene chloride, which was washed with 250 ml of 10% sodium carbonate solution and dried with MgSO_4 . The methylene chloride was removed by rotary evaporation, and the residual material was distilled under reduced pressure. A yellow liquid was obtained with a boiling point of 90-2° (3 mm) (22 g/41%) [lit.⁵⁴ 91-2° (4 mm)].

Preparation of 1-, 2-, and 3-chlorocycloheptatriene.¹⁶

In a 100 ml three-necked round-bottomed flask equipped with a drying tube addition funnel and a nitrogen inlet was stirred, in an ice bath, 2.0 g of tropone (19 mmol) in 12 ml of CH_2Cl_2 under nitrogen. To this was added dropwise, over 15 minutes, 2.5 g (20 mmol) of oxalyl chloride in 4 ml

of CH_2Cl_2 . The resulting slurry was stirred for an additional 35 minutes. With minimal exposure to air, the solvent was removed by rotary evaporation.

In the same flask, the yellow residue was dissolved in 45 ml of dry THF and the flask was equipped with a drying tube, a nitrogen inlet, and a solid addition tube containing 1.49 g of lithium aluminum hydride. The system was purged with nitrogen and cooled in an ice bath. The lithium aluminum hydride was added in small portions, with stirring over 15 minutes. The resulting suspension was stirred for an additional hour and allowed to come to room temperature. The excess hydride was destroyed with water and the precipitated material filtered. The mother liquor was extracted with 250 ml of CH_2Cl_2 and dried with MgSO_4 . The solvent was removed by rotary evaporation and the resulting liquid purified by column chromatography on silica gel using pentane as the elutant. The resulting yellow oil (1.5 g, 60% yield) was a mixture of 1-, 2-, and 3-chlorocycloheptatriene, that had the nmr spectrum reported in the literature.¹⁶

Preparation of zinc copper couple.¹⁷ To 2.0 g of cupric acetate dissolved in 50 ml of glacial acetic acid in a 125 ml Erlenmeyer flask heated to 100° and stirred magnetically, was added in one portion, 35 g of zinc dust. The slurry was shaken well and an additional 50 ml portion of acetic acid was added. When the material had cooled, the acetic acid was decanted from the resulting red-grey solid. This solid was washed three times with 100 ml of ether and stored under ether.

The reactivity of the above couple was tested by reacting it with methylene iodide in the presence of cyclohexene. In a 50 ml round-bottomed flask equipped with a reflux condenser and magnetic stirrer, was placed ca. 7 g of the wet couple and 20 ml of ether. To this was added ten drops of CH_2I_2 which resulted in evolution of bubbles from the solvent. A mixture of 5 g of cyclohexene and 13 g of CH_2I_2 was then added dropwise over 15 minutes. When the initial reaction subsided, the material was refluxed overnight. The slurry was then filtered and the solid washed with 25 ml of 1N HCl, which was added to the ether. The layers were separated and the ether was washed three times with water and dried with MgSO_4 . The nmr spectrum of the residual material after removal of the ether by distillation showed the presence of norcarane.

Attempted reaction of 1-, 2-, and 3-chlorocycloheptatriene. In a 50 ml round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 320 mg of the above couple in 20 ml of ether. To this was added 0.5 g (4 mmol) of the chloride mixture in 1.1 g (4.1 mmol) of CH_2I_2 , and the resulting slurry refluxed overnight. The precipitated material was filtered off and washed with 10 ml of 1N HCl which was used to wash the supernatant ether solution. The ether was washed with an additional 10 ml portion of 1N HCl solution and then three times with 10 ml of water. The ether was then dried with MgSO_4 . Evaporation

of the ether yielded a yellow oil shown by nmr and tlc to be only the starting mixture of chlorocycloheptatrienes.

Repetition of the above reaction with extended reflux times yielded the same results.

Preparation of 7,7-dibromobicyclo[4.1.0]-2-heptene.¹⁸

In a 500 ml three-necked round-bottomed flask equipped with a mechanical stirrer addition funnel and nitrogen purge, cooled in an ice bath, were stirred 200 ml of pentane, 24 g (0.29 mol) 1,3-cyclohexadiene and 33.7 g (0.30 mol) potassium t-butoxide. To this slurry was added with efficient stirring, 75.8 g (0.30 mol) of bromoform in 90 ml of pentane, dropwise over 2 hours. The slurry was allowed to stir an additional 4 hours at 0°, and allowed to warm to room temperature overnight. To this was then added 400 ml of water and the layers were separated. The aqueous phase was then extracted twice with 200 ml of pentane. The combined pentane extracts were then washed two times with 200 ml of water and dried over MgSO₄. Removal of solvent by rotary evaporation leaves an oil that is purified by reduced pressure distillation. Thirty-seven grams of liquid [bp 80-2° (5 mm), 68-70° (.8 mm)] (49% yield) was collected. The identity of this compound was confirmed by comparison of its nmr with that recorded in the literature.¹⁸ This material was stable over a period of weeks if kept refrigerated.

Preparation of 2- and 3-bromocycloheptatriene.¹⁸ In a 250 ml three-necked round-bottomed flask equipped for distillation through a short Vigreux tube into a receiver

cooled in an ice bath, 72 g of quinoline was heated to 135-45°. The system was then evacuated via a water aspirator, and 24.3 g (96.4 mmol) of the above dibromide was added dropwise. The system was adjusted by a nitrogen bleed so that a rapid distillation of the resultant bromide occurred with only limited co-distillation of the quinoline. The distillate was then chromatographed on silica gel, eluting with pentane, to yield 9.32 g (57%) of yellow oil, identified as a mixture of 2- and 3-bromocycloheptatriene by nmr. The isomer composition of the 2- and 3- isomers determined by integration of the methylene signals of the nmr spectrum is 3 to 1, respectively [bp 74° (15 mm), lit.¹⁸ 76-8° (16 mm)].

Preparation of 2- and 3-cycloheptatrienyl formaldehyde.

In a 500 ml round-bottomed flask equipped with a low temperature thermometer, an argon inlet and septum, 6.8 g (0.40 mol) of the mixture of 2- and 3-bromocycloheptatriene was dissolved in 150 ml of dry THF. Under an argon blanket, this solution was cooled to -70° by immersion in a dry ice bath while stirring magnetically. To this was added dropwise at a rate that allowed the temperature to remain below -65°, 31 ml of n-butyllithium (1.6 M in hexane) (0.05 mol). Stirring was continued for an additional 20 minutes at -70°. Then a solution of 7.3 g (0.10 mol) of dry dimethylformamide in 50 ml of THF was added dropwise at a rate that allowed the temperature to remain below -65°. Again the solution was stirred for 90 minutes at -70°; then it was allowed to warm

to -20° . One hundred milliliters of saturated NH_4Cl solution was added and the mixture was filtered, separated, and the aqueous phase was extracted three times with 100 ml of ether. The combined organic phases were washed five times with ice in water and dried with NaSO_4 . The solvent was removed by rotary evaporation and the residue was purified by chromatography on silica gel, utilizing pentane to elute a fast-moving impurity, ultimately eluting the aldehyde with 25% ether in pentane. A yellow oil (2.6 g, 55%) was obtained that was identified by nmr as the aldehydes named above, in the same ratio as the starting bromides.

^1H NMR (CDCl_3) 2.5 (t), 2.4 (t), 5.2-7.4 (m), two singlets 569 and 574 Hz downfield from TMS.

Preparation of cycloheptatrienyl formaldehyde tosylhydrazones. In a round-bottomed flask under nitrogen, 2 g of the above aldehyde was stirred with 3.1 g of tosylhydrazide in 30 ml of absolute ethanol for 1.5 hours. On silica gel using CH_2Cl_2 as the eluting solvent, TLC showed almost complete conversion to tosylhydrazone. Removal of the ethanol by rotary evaporation yielded a glass that was recrystallized twice from ether, yielding 3.6 g (72%) of crystals that tended to retain ether. The ether was removed by chromatography on silica gel with methylene chloride.

^1H NMR (CDCl_3) 2.3 (m), 2.35 (s), 5.2-7.5 (m), 7.5 (A_2X_2), two singlets 513 and 520 Hz downfield from TMS.

Preparation of the sodium salts of the cycloheptatrienyl formaldehyde tosylhydrazones. Under a nitrogen atmosphere in a dry box, 576 mg (12 mmol) of NaH (50% in oil) was added to 3.5 g of the above tosylhydrazone mixture in 40 ml of dry THF. After stirring for 15 minutes, 40 ml of hexane was added to precipitate the salt. This was filtered and washed twice with 10 ml of hexane. After drying under nitrogen, 2.53 g of material that decomposed between 165-75° was obtained.

Pyrolysis of the sodium salts of the cycloheptatrienyl formaldehyde tosylhydrazones. In a 25 ml round-bottomed flask equipped with a solid addition funnel and a reflux condenser, 15 ml of diglyme was refluxed under nitrogen. To this was added in portions 310 mg of the sodium salt. The resulting slurry was refluxed for 30 minutes and then poured into 100 ml of water. This was extracted three times with 75 ml of pentane and then three times with 75 ml of ether. The ether was washed with water (10 x 100 ml) and dried over MgSO_4 . Evaporation of the ether yielded a brown oil (40 mg, 30%) that was shown to contain the pyrazoles 6 and 7.

^1H NMR (CDCl_3) 7.5 (s), 7.6 (s), 6.5-6.8 (m), 3.5 (d, $J = 6$ Hz), 2.7 (t, $J = 6$ Hz); mass spectrum m/e (rel intensity) 132(21.1), 131(28.0), 105(15.3), 104(9.0); high resolution mass spectra m/e 132.06785, theoretical: 132.06870.

Photolysis of the sodium salts of the cycloheptatrienyl formaldehyde tosylhydrazones. To 125 ml of dry THF in a Pyrex immersion well, irradiated (550 W, Hanovia medium

pressure lamp) under nitrogen, was added with efficient stirring, 310 mg of the sodium salt over 20 minutes. Photolysis was continued for 2.5 hours yielding a yellow mixture. The solvent was removed by rotary evaporation, and the residue was washed three times with 10 ml of methylene chloride. The remaining solid weighed 115 mg. (A quantitative yield of sodium toluene sulfinat would have been 178 mg.) The solvent was evaporated from the methylene chloride fraction, and the resulting material was chromatographed on silica gel with chloroform/methanol 3:2. A yellow band was eluded yielding an oil (87 mg, 66%) that was shown by mass spectroscopy to be isomeric with the pyrazoles isolated from the pyrolysis of the salt. The proton spectrum shows them to be different compounds.

^1H NMR (CDCl_3) 7.5 (s), 7.3 (s), 5.5-6.5 (m), 2.8 (d, \underline{J} = 5 Hz), 2.8 (t, \underline{J} = 4 Hz); mass spectrum m/e (rel intensity) 132(99.7), 131(100), 105(21.7), 104(23.1); IR (major peaks) 3200, 3000, 2900, 1700, 1600, 1180.

Preparation of 8-chlorobicyclo[5.1.0]2,4-octadiene (10).

In a 1 liter three-necked round-bottomed flask equipped with an addition funnel and a dry ice condenser 175 g (1.90 mol) of freshly distilled cycloheptatriene and 55 g of methylene chloride (0.65 mol) were stirred in 200 ml of ether under nitrogen. To this was added dropwise 200 ml (1.77 M, 0.35 mol) of methyllithium in ether over 1.5 hours. The ether refluxed. The material was allowed to cool to room temperature while stirring was continued for an additional

two hours. The resulting slurry was poured into 250 ml of water to dissolve the precipitated material. The layers were separated and the aqueous layer was extracted three times with 200 ml of ether. The organic phases were combined and dried over MgSO_4 . The ether was removed by rotary evaporation, and the residual cycloheptatriene was removed by bulb to bulb distillation at 10 mm. The remaining oil was distilled through a Vigreux column at 5 mm. The fraction boiling at 52-60° was collected yielding 11 g of yellow oil (22%). This oil was distilled through a spinning band column with no apparent change in the nmr [bp 57-8° (3 mm)].

^1H NMR (CDCl_3) 5.9 (m), 5.7 (m), 3.6 (t, \underline{J} = 3 Hz), 3.0 (t, \underline{J} = 8 Hz), 2.5 (m), 1.6 (m); mass spectra m/e (rel intensity) 140(10.1), 105(100), 91(29.2); high resolution mass spectrum m/e 140.0392, theoretical: 140.0392; IR (major peaks) 3050, 3000, 1620, 1440, 1380, 1280, 1240, 1050, 840, 760.

Anal. Calcd for $\text{C}_8\text{H}_9\text{Cl}$: C, 68.34; H, 6.45. Found: C, 68.23; H, 6.46.

Reaction of 8-chlorobicyclo[5.1.0]2,4-octadiene (10) with maleic anhydride. In a 200 ml round-bottomed flask, 1.000 g (7.1 mmol) of 10 and 0.7 g (7 mmol) of maleic anhydride were refluxed in 100 ml of carbon tetrachloride for 2 days. The solvent was evaporated and the residue was dissolved in a minimum amount (30 ml) of hot carbon tetrachloride. Upon cooling, crystals formed. These were separated and the mother liquor was concentrated to half its

original volume by heating on a steam cone. A second crop of crystals was taken. Combination of these two crops yielded 513 mg of white crystals that decomposed at 164° (sealed tube). The mother liquor was chromatographed on silica gel, eluting with pentane. The fast running fraction corresponding to 10 was collected. Evaporation of the solvent resulted in the recovery of 246 mg of 10. Correcting for the recovered starting material, the yield of adduct was 45%.

^1H NMR (CDCl_3) 6.5 (m, 2H), 3.8 (m, 1H), 3.4 (d, 2H), 3.0 (m, 2H), 2.8 (m, 2H), 2.3 (m, 2H); mass spectrum m/e (rel intensity) 238(1.4), 166(3.5), 150(2.7), 131(3.4), 78(100); IR (major peaks) 3500, 3000, 1850, 1775, 1220, 1080, 960, 920, 900, 785.

Preparation of 8,8-Dibromobicyclo[5.1.0]2,4-octadiene²⁴
(17). In a 2 liter Morton flask equipped with a mechanical stirrer and cooled in an ice bath, 96 g (1.0 mol) of cycloheptatriene and 151 g (0.60 mol) of bromoform were stirred in 200 ml of pentane, under nitrogen. Over a period of 1.5 hours, 56 g (0.50 mol) of potassium *t*-butoxide was added in small portions. The resulting slurry was allowed to come to room temperature and was stirred overnight. This material was added to 300 ml of water and the layers were separated. The aqueous layer was extracted two times with 250 ml of methylene chloride. This was added to the pentane fraction and the combined organics were washed with 200 ml of water and dried over MgSO_4 . The solvent was removed by rotary

evaporation and the remaining cycloheptatriene and bromoform were removed by bulb to bulb distillation at 5 mm. The pressure was lowered to 0.05 mm and the remainder of the material was distilled from a steam bath into a vessel cooled in dry ice. This material was quickly distilled again at 0.05 mm, collecting a fraction boiling above 50°. This was chromatographed on silica gel, eluting with pentane, to yield 33 g (24%) of yellow liquid whose nmr matches that reported in the literature for 17²⁴ [lit. bp 42-6° (0.02 mm)]²⁴ This material darkened at storage temperatures below 0°, but its properties were not affected.

¹H NMR (CDCl₃) 5.1-6.3 (m, 4H), 2.3-2.6 (m, 2H), 2.1-2.4 (m, 2H).

Reduction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17)
with tri-n-butyltin hydride. The tri-n-butyltin hydride was prepared by the method of Kuivila⁵⁵ and used as soon as possible after preparation. In a 25 ml pear-shaped flask with a septum top, 3.0 g (11 mmol) of the dibromide was stirred magnetically under nitrogen. To this was added dropwise, via syringe, 3.3 g (11 mmol) of the fresh hydride. This was stirred for 24 hours and then distilled under reduced pressure through a Vigreux column, collecting a fraction boiling between 55 and 60° (1 mm). This material was contaminated with tri-n-butyltin bromide, and so was chromatographed on silica gel, eluting with pentane. A fast running band was taken that yielded 500 mg of an oil,

still contaminated with the tin bromide, with an nmr similar to that of 10.

^1H NMR (CDCl_3) 5.3-6.2 (m), 3.5 (t, $J = 4$ Hz), 3.0 (t, $J = 8$ Hz), 2.0-2.6 (m), 1.4-1.8 (m); mass spectrum m/e (rel intensity) 186(4.2), 184(10.8), 182(7.8), 105(100), 91(51.2); IR (major peaks) 2970, 2870, 1800, 1590, 1480, 1440, 1420, 1360, 1300, 1240, 1200, 1060, 1030, 870, 840, 800.

Reaction of 8-chlorobicyclo[5.1.0]2,4-octadiene (10) with potassium t-butoxide, general procedure. In a 100 ml three-necked flask, 5.0 g (45 mmol) of potassium t-butoxide was stirred under nitrogen in 50 ml of dry THF. If a trap was used, it was added to this solution. This solution was then allowed to come to the desired temperature, and a solution of 700 mg of the chloride, 10, in 20 ml of THF was added dropwise. Stirring was continued for one hour and the resulting material was poured into 100 ml of water. This was extracted three times with 75 ml of pentane, which was washed three times with 100 ml of water to remove any remaining THF. The pentane solution was dried over MgSO_4 . The solvent was evaporated and the material chromatographed on silica gel, eluting with pentane. A fast running band was taken, which was shown to contain cyclooctatetraene and styrene, by nmr and gas chromatography (11.5' 10% SE-52, 90°).

Yields [corrected to reactive isomer, (12)]

T°	COT	Styrene	
25°	56%	trace	
65°	36%	4%	
90°	8%	8%	(solvent: tetraglyme)

Yields were determined by gas chromatography using p-methylstyrene as an internal standard. Styrene was not generated from the reaction of cyclooctatetraene with potassium t-butoxide under the above conditions.

Preparation of 8-chlorobicyclo[5.1.0]2,4-octadiene (10) enriched in 11. In a 50 ml round-bottomed flask, under nitrogen, 1.4 g (10 mmol) of the mixture of chlorides was stirred in 20 ml of dry THF. To this was added dropwise, at room temperature, 270 mg (2.5 mmol) of potassium t-butoxide in 20 ml of THF. The solution was stirred for 45 minutes and then poured into 100 ml of water. The phases were separated, and the aqueous layer was extracted three times with 50 ml of pentane. The combined extracts were washed three times with water (300 ml) and dried over MgSO_4 . Evaporation of the solvent and chromatography on silica gel, eluting with pentane, yielded 818 mg of yellow oil. The oil was pumped overnight at 1 mm to remove cyclooctatetraene, yielding 410 mg of almost pure 11 (92% isomer purity by nmr integration of the triplets at 3.0 and 3.6) containing no cyclooctatetraene.

Reaction of 8 chlorobicyclo[5.1.0]2,4-octadiene (10) with potassium t-butoxide at 90°/1 mm. In a 100 ml round-bottomed flask equipped with a septum and connected to a vacuum system through a Vigreux column and a trap cooled in liquid nitrogen, was stirred 5.0 g (45 mmol) of potassium t-butoxide in 40 ml of tetraglyme. The cooled trap had previously been charged with 0.1 ml of dimethyl acetylene

dicarboxylate in 10 ml of THF. With stirring, the flask was evacuated (0.5-1 mm) and heated in an oil bath (90-5°). When the system had come to temperature, a solution of 1.4 g (10 mmol) of 10 in 20 ml of tetraglyme was injected dropwise through the septum via syringe. With the first addition of chloride a red material began to collect in the cold trap. After the addition was complete the black solution was allowed to react for an additional hour, although no additional reaction was apparent. Nitrogen was bled into the system, and the red material was washed into the trap with a solution of 0.2 ml of the diester in 10 ml of THF. This solution was placed in the refrigerator for 24 hours, during which the color changed from red to orange. After 48 hours, the solution was almost yellow. After 72 hours in the refrigerator the solution was reduced to one-fourth its original volume on the steam cone. Benzene (25 ml) was added, and this solution was reduced in volume in the same manner. Benzene was then added to make the solution to 25 ml, and 0.5 g of Pd on charcoal was added. Air was bubbled through this mixture overnight, after which the catalyst was removed by filtration through a small column of alumina, washing well with ether. The resultant material was chromatographed on deactivated alumina, eluting with ether to bring down a yellow band. Elution with methanol yielded a purple material which was purified further by TLC (alumina/ether), to yield a blue material.

UV/VIS (C_6H_{12}) 575, 365, 347, 305, 290, 235; lit.³³ 580, 370, 350, 300, 290, 240; mass spectrum m/e (rel intensity) 244(50.3), 213(100), 183(32.6).

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17) with potassium t-butoxide at 0°. In a 100 ml round-bottomed flask, equipped with an addition funnel and immersed in an ice bath, was stirred a solution of 5.0 g (45 mmol) of potassium t-butoxide in 25 ml of THF. To this was added dropwise a solution of 1.32 g (5.0 mmol) of 17 in 20 ml of THF. This was stirred at 0° for 30 minutes and allowed to come to room temperature. This was poured into 300 ml of water, and the resulting solution was extracted three times with 100 ml of pentane. Subsequent extraction of the aqueous phase with ether yielded nothing. The combined pentane extractions were combined and washed three times 100 ml of water and dried over $MgSO_4$. The residue was chromatographed on silica gel plates (1.5 mm, activated at 140° for 30 minutes). Two bands (R_f .3 and .5 were isolated after elution with pentane for three cycles. These two fractions (R_f = .5, 45 mg; R_f = .3, 35 mg) had nmr and mass spectral characteristics of t-butyl styryl ethers.

For R_f = .5 (trans isomer) 1H NMR ($CDCl_3$) 7.2 (s), 7.1 (d, J = 12 Hz), 6.0 (d, J = 12 Hz), 1.4 (s); mass spectrum m/e (rel intensity) 176(3.0), 120(100), 91(37.4), 77(3.4).

For $R_f = .3$ (cis isomer) $^1\text{H NMR}$ (CDCl_3) 7.0-7.8 (m), 6.5 (d, $\underline{J} = 7$ Hz), 5.3 (d, $\underline{J} = 7$ Hz), 1.4 (s); mass spectrum m/e (rel intensity) 176(3.8), 120(100), 91(40.3), 77(3.5).

Preparation of 3-phenylphthalide.⁵⁶ In a 2 liter round-bottomed flask equipped for reflux, 200 g of zinc dust, 100 g (0.44 mole) o-benzoylbenzoic acid, 200 ml of water, and 800 ml of glacial acetic acid were refluxed vigorously for 2 hours. The resultant yellow solution was decanted from the residue, which was washed with 200 ml of hot glacial acetic acid. The solutions were combined and allowed to stand overnight. Beautiful white needles were separated by filtration. Addition of 500 ml of water to the mother liquor generated a second crop, and addition of another 500 ml of water, followed by cooling in ice, allowed a third crop to be collected. These combined crystals were added carefully in portions to 600 ml of 5% NaHCO_3 solution with stirring. Stirring was continued for an additional hour to allow the flocculent material to digest. This was filtered and recrystallized from 800 ml of hot ethanol. Hot filtration was necessary to remove an insoluble impurity. After two crops, 51 g of material was isolated (mp 114-5°, lit.⁵⁶ 115-6°) (55%). Additional material of questionable purity could be isolated (10 g) but was not retained.

Preparation of 1,3-diphenylisobenzofuran.³⁷ In a 250 ml addition funnel capped at the bottom with a 50 ml round-bottomed flask, and equipped with a reflux condenser,

phenylmagnesium bromide was generated under nitrogen from 40 g of bromobenzene and 6 g of magnesium turnings.

The funnel was transferred to a 1 liter three-necked round-bottomed flask and the Grignard was dripped into 42 g of 3-phenylphthalide in 250 ml of dry THF over a period of 45 minutes. After an additional hour of stirring, 250 ml of benzene was added, and the resulting solution was washed two times with 250 ml of 1N HCl. The organic phase was then washed with 100 ml of 10% K_2CO_3 . The aqueous phases were then combined and extracted with 100 ml of benzene. The combined organics were filtered through a frit containing $MgSO_4$. The solvent was evaporated and the residue was recrystallized from 250 ml of hot benzene. A second crop was precipitated by addition of 200 ml of ethanol. The combined solids were again recrystallized from benzene to yield 38 g (70%, lit.³⁷ 87%) of yellow needles melting at 128-30° (lit.³⁷ 130-1°).

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17) with potassium t-butoxide and 1,3-diphenylisobenzofuran, general procedure. In a 100 ml round-bottomed flask equipped with an addition funnel and nitrogen inlet, was stirred 5.0 g (45 mmol) of potassium t-butoxide and 1.35 g of 34 (5.0 mmol) in 40 ml of dry THF. Under a blanket of nitrogen, the solution was brought to the desired temperature. A solution of 1.32 g (5.0 mmol) of 17 in 20 ml of THF was added dropwise, and after addition was complete, the solution was allowed to stir for an hour. Ether (100 ml)

was added and the phases separated. The aqueous phase was extracted three times with 100 ml of ether. The organic phases were combined and washed four times with 100 ml of water and dried over MgSO_4 . The solvent was removed by rotary evaporation and the resulting solid pumped overnight at 1 mm to remove any traces of THF. This material was chromatographed on silica gel, eluting with carbon tetrachloride, taking the adduct as a freely moving band.

Reaction of 8-chlorobicyclo[5.1.0]2,4-octadiene (10) with potassium t-butoxide and 1,3-diphenylisobenzofuran at -78° . A solution of 2.8 g of 10 (20 mmol, 5 mmol of 12) in 20 ml of THF was allowed to react with 5.0 g (45 mmol) of potassium t-butoxide and 1.35 g (5.0 mmol) of 34 in the manner described for the general reaction of 17. After the addition of 10 was complete and the resulting solution was stirred for one hour, a solution of maleic anhydride in THF was added until tlc (silica gel/pentane) showed that the 34 was consumed. Work up was then resumed in the general manner. Chromatography on silica gel, eluting with CCl_4 , yielded a crystalline material as the second material eluted from the column. (The first material eluted was unreacted 11 and some cyclooctatetraene.) Recrystallization from benzene/methanol yielded 197 mg (11%) of white crystals, melting at $168-9^\circ$. Two more recrystallizations yielded an analytically pure material, mp $169-169.5^\circ$.

^1H NMR (CDCl_3) 7.0-8.0 (m, 14H), 5.8-6.2 (m, 4H), 2.1-3.2 (m, 3H), 1.7 (d, $J = 4$ Hz, 1H); mass spectrum m/e

(rel intensity) 374(5.7), 270(100), 91(6.9), 77(16.8); high resolution mass spectrum m/e 374.16865, theoretical 374.16706; ir (major peaks) 3050, 2970, 2900, 1590, 1480, 1430, 1330, 1280, 1040, 1020, 970, 910, 900.

Anal. calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.71; H, 6.01.

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17) with potassium t-butoxide and 1,3-diphenylisobenzofuran at -78° . Silica gel chromatography (CCl_4) of the material formed at -78° by the above procedure allowed a moderately slow moving material to be separated from a small amount of rapidly eluted 34. After evaporation of the solvent, 1.157 g of material was isolated that was shown to be 19. Three recrystallizations from THF/pentane gave an analytically pure sample (mp $156-7^\circ$) whose nmr did not differ from the material separated by chromatography (51% yield).

1H NMR ($CDCl_3$) 7.2-8.0 (m, 14H), 5.8-6.5 (m, 3H), 5.5 (d, $J = 10$ Hz, 1H), 3.0-3.4 (m, 1H), 2.5-2.9 (m, 2H); mass spectra m/e (abs intensity) 20 eV 454(32), 452(47), 373(50457); (rel intensity) 70 eV 373(100); ir (major peaks) 3080, 3050, 2960, 2940, 1510, 1460, 1350, 1310, 1150, 1120, 1000.

Anal. Calcd for $C_{28}H_{21}BrO$: C, 74.18; H, 4.67. Found: C, 73.99; H, 4.72.

Preparation of 8,8-dichlorobicyclo[5.1.0]2,4-octadiene. In the same manner as the preparation of 17, 120 g (1 mole) of chloroform and 100 g (1.1 mole) of cycloheptatriene were

allowed to react with 52 g of potassium t-butoxide (.5 mol) Work up in the same way yielded 12.4 g (14%) of oil boiling at at 45° (0.05 mm) [lit.⁵⁷ 36-9° (0.05 mm)].

¹H NMR (CDCl₃) 5.5-6.4 (m, 4H), 2.4-2.6 (m, 2H), 2.0-2.4 (m, 2H); mass spectrum m/e (rel intensity) 178(1.5), 176(5.7), 174(7.3), 139(62.3), 103(100), 91(21.4).

Reaction of 8,8-dichlorobicyclo[5.1.0]2,4-octadiene with potassium t-butoxide and 1,3-diphenylisobenzofuran at -78°. Silica gel chromatography (CCl₄) of the material formed at -78° by the general procedure allowed a material very similar to the 34 adduct of the cyclopropene formed from 17 to be isolated. This solid (0.792 g, 39% yield) was recrystallized from THF/pentane to yield a material with a melting point of 148.5-150°.

¹H NMR (CDCl₃) 7.1-7.9 (m, 14H), 5.8-6.5 (m, 3H), 5.5 (d, J = 11 Hz, 1H), 3.0-3.5 (m, 1H), 2.5-2.9 (m, 2H); mass spectra m/e (abs intensity) 20 eV 408(131), 410(46), 373(39475); (rel intensity) 70 eV 373(100).

Anal. Calcd for C₂₈H₂₁ClO: C, 82.24; H, 5.18. Found: C, 80.73; H, 5.36.

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17) with potassium t-butoxide and 1,3-diphenylisobenzofuran at 0°. The reaction was repeated via the general procedure at 0°. Chromatography yielded a material (22) that was eluted with CCl₄ in the usual manner. Another material (23) was eluted with ether. This material appeared to have been spread throughout the length of the column during the

elution with CCl_4 . This compound, 23, was not apparent in the nmr of the crude material before chromatography. This crude material (1.99 g) appeared to be almost totally composed of 22. Determination of the composition of this crude material by nmr, using 1,3,5-trinitrobenzene as the internal standard, showed it to contain 2.57 mmol (1.16 g, 51%) of 22. Two recrystallizations of the material eluted with CCl_4 in benzene/methanol yielded 335 mg of a labile white material that darkened at 95° and decomposed at 110° . Recrystallization of 23 from chloroform/methanol yielded crystals melting at $200-1^\circ$ (340 mg).

For 22, ^1H NMR (CDCl_3) 7.7-8.0 (m), 7.3-7.5 (m), 7.2 (s), (14H); 5.2-6.5 (m, 6H); 4.5 (s, 1H). Mass spectrum m/e (rel intensity) 454(.5), 452(.4), 267(100). High resolution mass spectrum m/e 454.07642, theoretical, 454.07540. IR (major peaks) 2950, 1550, 1460, 1420, 1410, 1310, 1270, 980.

For 23 ^1H NMR (CDCl_3) 7.0-7.7 (m, 19H), 5.5 (s, 1H); mass spectrum m/e (rel intensity) 372(1.7), 267(100); high resolution mass spectrum m/e 372.15138, theoretical 372.15130; ir (major peaks) 3100, 1670, 1605, 1595, 1500, 1450, 1000.

Anal. calcd for $\text{C}_{28}\text{H}_{20}\text{O}$: C, 90.29; H, 5.41. Found: C, 90.43; H, 5.46.

Preparation of 1,2,4-triphenyl-1,4-butandione.⁴⁰ In a 500 ml round-bottomed flask, 18 g of acetophenone and 31 g of benzoin were refluxed with 4 g of KCN in 75 g of water

and 75 g of ethanol. After boiling for a half hour, an oil began to form. After 1.25 hours, the oil was separated and the mother liquor was allowed to stand. More oil was collected and combined with that previously obtained. After this material had stood for 1.5 hours and had begun to solidify, it was transferred to porous tiles, where it immediately crystallized. This material was boiled in 300 ml of ethanol and filtered hot. The mother liquor was allowed to stand, and crystals formed. The residue was added to 300 ml of ethanol and refluxed for a half hour. This was filtered while hot and allowed to stand until crystals formed. The two sets of crystals were combined to yield 22 g (40%) of yellow crystals that were used without further purification.

Preparation of 2,3,5-triphenylfuran.⁴⁰ In a 250 ml Erlenmeyer flask, the above crystals were stirred in 150 ml of concd H_2SO_4 , for two hours. This was poured onto 1000 ml of ice. The sticky material was separated and dissolved in 200 ml of boiling ethanol. When cooled, this precipitated white needles (16.2 g, 78%), that melted at $90-1.5^\circ$ (lit.⁴⁰ 92°).

Reaction of triphenylfuran with benzyne. In a 250 ml Erlenmeyer flask, 6.8 g (.05 mol) of anthranilic acid was dissolved in 75 ml of ethanol and 5 ml of concd HCl and cooled in an ice bath to $0-5^\circ$. With stirring, 12.5 ml (.093 mol) of isoamyl nitrite was added dropwise at a rate keeping the temperature below 10° . After ten minutes of

stirring, a precipitate formed. Ether (75 ml) was added and the solid material filtered and washed with ether.

Five grams (.27 mol) of this material, along with 8 g of 2,3,5-triphenylfuran and 3 g of propylene oxide (acid scavenger) was refluxed in 50 ml of dichloroethane for 3 hours. After cooling the solvent was removed by rotary evaporation. The residual material was chromatographed on silica gel, eluting with pentane. The residual triphenylfuran was removed as a fast running band. Elution with ether allowed collection of a solid material after evaporation of the solvent. This material was recrystallized from THF/pentane to yield 3 g of crystals melting at 170-5°. Additional recrystallizations from CCl₄ yields a colorless material melting at 172-4°.

¹H NMR (CDCl₃) 7.0-8.0 (m); mass spectrum m/e (rel intensity) 372(36.7), 270(100), 261(60.0); ir (major peaks) 3050, 2950, 1590, 1480, 1430, 1330, 1290, 1040, 995, 980.

This material was inert in acetonitrile solution, and does not show any evidence of being converted to 23 after overnight reflux in acidic methanol overnight.

Reaction of 8,8-dibromobicyclo[5.1.0]2,4-octadiene (17) with potassium t-butoxide with subsequent addition of 1,3-diphenylisobenzofuran. As in the general procedure, 1.32 g of 17 was allowed to react with 5.0 g of base, without 34, at -78°. After an hour of stirring at this temperature, 1.35 g of 34 in 20 ml of THF was added dropwise over 10 minutes, and the resulting solution was allowed to warm

to room temperature. After the usual work up with ether and water, a large amount of polymer was noted. The nmr spectrum of the crude material showed some 22 and no bromocyclo-octatetraene. There was also no evidence of the styrene ethers.

Preparation of coumalic acid.⁴⁸ In a 2 liter round-bottomed flask at room temperature 200 g (1.5 mol) of DL-malic acid was stirred magnetically in 170 ml of concd H_2SO_4 . To this was added carefully, in one portion, 50 ml of fuming H_2SO_4 , and the mixture was allowed to stir for 45 minutes. This procedure was repeated twice (total, 150 ml fuming H_2SO_4). After the last addition of acid the material was allowed to stir for one hour and was transferred to the steam cone, where it was heated for 2 hours. After a slight cooling period, the warm solution was poured carefully onto 800 g of ice. This was allowed to stand overnight. The solid was filtered and washed three times with 300 ml of ice cold water. The solid was dried on a sand bath at 65° , and divided into two portions. One of these portions was recrystallized from 170 g of methanol, decolorizing with Norite. The solid was separated and the mother liquor was used to recrystallize the other portion. This resulted in 45 g of sulfur yellow crystals (22%) melting at $206-9^\circ$ (lit.⁴⁸ $206-9^\circ$).

Preparation of 2-pyrone.⁴⁹ Coumalic acid (30 g, .21 mol) was sublimed at 0.5 mm through a Vycor tube packed loosely with copper turnings and heated to 650° . The

resulting yellow oil was collected in an ice-cooled trap. Distillation of this oil at 26 mm yielded 12.3 g of material boiling between 106° and 109° [lit.⁴⁹, 110° (26 mm)]. This material was stored under nitrogen below 0° until used.

Preparation of the sodium salt of tropone tosylhydrazone. The sodium salt of tropone tosylhydrazone was prepared by the method of Jones and Ennis,⁵¹ by the reaction of tropone tosylhydrazone with sodium hydride in THF. The resulting precipitate was recrystallized from 1% DMSO in THF to yield purple needles.

Preparation of 6-chloro-2-pyrone.⁵³ To a 100 ml round-bottomed flask containing 10 g (0.077 mol) of glutamic acid and cooled in an ice bath, was added in portions 30 g (.14 mol) of phosphorous pentachloride. During the course of the addition, gas was evolved and the solids melted. When spontaneous reaction ceased, the solution was allowed to warm to room temperature. Again, reaction commenced and when this moderated, the material was heated for 15 minutes on a steam cone. The resulting red liquid was distilled yielding 7.1 g of material [bp 64-5° (.5 mm), lit.⁵³ 67° (9 mm)] identified by comparison with the nmr spectrum noted in the literature.⁵⁸

Preparation of 6-d-2-pyrone.⁵³ In a 50 ml round-bottomed flask containing 5.8 g (44 mmol) of 6-chloro-2-pyrone in 30 ml of THF, under nitrogen, was added 11.6 g (77 mmol) of vacuum-dried NaI. This was allowed to stand, with occasional swirling, for 4 hours. The resulting material

was poured into 20 ml of deuterioacetic acid and 30 g of zinc dust (vacuum dried at 130°). This was allowed to stand under nitrogen overnight, and then was poured into 100 ml of CH_2Cl_2 , filtered, and the resulting solid washed three times with 100 ml of water and two times with 10% Na_2CO_3 solution and dried over Na_2SO_4 . After chromatography on silica gel, eluting with CH_2Cl_2 and distillation from a bath at 115° (25 mm), 607 mg of material was isolated that was identified by comparison of the nmr⁵⁸ and mass spectrum⁵³ with the literature.

Pyrolysis of the sodium salt of tropone tosylhydrazone in the presence of 2-pyrone. Under nitrogen, 1.4 g (14 mmol) of 2-pyrone in 15 ml of dry diglyme was heated to 110°. In portions, 0.5 g (1.4 mmol) of the sodium salt was added through a solid addition funnel. Stirring was continued for 30 minutes at this temperature. The resulting material was poured into 150 ml of water and was then extracted three times with 100 ml of pentane. The pentane extracts were washed six times with 50 ml of water and dried over MgSO_4 . Chromatography (Fisher basic alumina, activity grade III/pentane) yielded 58.9 mg (29%) of material identified as 3,4-benzocycloheptatriene by comparison with the nmr reported in the literature.⁴¹

Pyrolysis of the sodium salt of tropone tosylhydrazone in the presence of 6-d-2-pyrone. In the same manner as the pyrolysis reported above, 100 mg (1.04 mmol) of 6-d-2-pyrone was allowed to react with the pyrolysis product of

the sodium salt of tropone tosylhydrazone (500 mg, 1.4 mmol). After the same type of work up, 33 mg of the 3,4-benzocycloheptatriene was isolated. The nmr spectrum showed that the deuterium was retained in the phenyl portion of the molecule.

^1H NMR (CCl_4) 2.50 (t, 1.8H, \underline{J} = 6 Hz), 5.82 (d of t, 2.1H, \underline{J} = 6, 10 Hz), 6.59 (d, 2.0H, \underline{J} = 10 Hz), 7.25 (s, 3.3H). Mass spectrum m/e (rel intensity) 144 (9.6), 143(90.0), 142(100), 116(26.9); for 3,4-benzocycloheptatriene 143(8.6), 142(79.4), 141(100), 115(29.8). IR (major peaks) 3010, 2950, 2820, 2220, 1480, 1450, 1430, 895, 820, 800.

Photolysis of the sodium salt of tropone tosylhydrazone in the presence of 2-pyrone. In a Pyrex photochemical immersion apparatus was stirred under nitrogen, 1.4 g (14 mmol) of 2-pyrone in 100 ml of dry THF. While irradiating with a 550 W Hanovia medium pressure lamp, 0.50 g of the sodium salt (1.4 mmol) was added in portions over 30 minutes. The mixture was worked up in the same manner as the pyrolyses. The average yield for the photolyses was 25 mg. The ratio of the 3,4-benzocycloheptatriene to 1,2-benzocycloheptatriene was 2:1.

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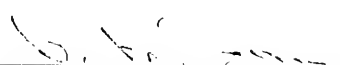
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BIOGRAPHICAL SKETCH

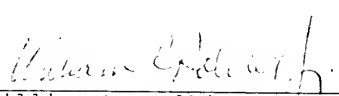
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